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XXV. *On the Viscosity and Molecular Dimensions of Gaseous Carbon Oxysulphide (COS).* By C. J. SMITH, B.Sc., A.R.C.S., D.I.C., Research Student, Imperial College of Science and Technology*.

THE present research is a continuation of the work on the measurements of the viscosities of gases, for the purpose of elucidating the structure of the molecules constituting them. Some measure of success has attended this investigation in many cases where the necessary data are known, and suggests that an accumulation of further similar data may be fruitful. A case in point is that of the molecule of carbon oxysulphide, and this paper describes the measurements of the viscous properties of this substance, which is ordinarily gaseous. The data, hitherto unknown, which have been obtained, have been applied to calculate the molecular dimensions in the ordinary way.

Apparatus and Method of Observation.

The apparatus and method, which have been used to determine the viscosity of carbon oxysulphide, have recently been fully described †.

Method of Experiment.

The viscometer was carefully standardized with a new mercury pellet in the manner indicated in previous papers.

* Communicated by Prof. A. O. Rankine, D.Sc.

† A. O. Rankine and C. J. Smith, *Phil. Mag.* vol. xlii. p. 601, Nov. 1921, and C. J. Smith, *Proc. Phys. Soc.* vol. xxxiv. p. 155, June 1922.

and the corrected time of fall proved to be 104.70 secs., a value which is probably correct to 0.1 sec. With this time of fall the corresponding time of fall for carbon oxysulphide has been compared, and with appropriate corrections gives the relative viscosity, from which the absolute viscosity has been obtained by assuming the viscosity of air at 15° C. to be 1.799×10^{-4} C.G.S. units. In addition, the variation of viscosity with temperature has been derived from comparisons of the corrected times of fall at atmospheric and steam temperature.

Preparation and Purification of the Carbon Oxysulphide.

The carbon oxysulphide was prepared by the action of sulphuric acid (five vols. acid, four vols. water) on pure potassium thiocyanate in the cold (room temperature). At the same time hydrocyanic acid, formic acid, and carbon bisulphide are formed. To remove these impurities the method recommended by Moissan* was used. This consists in passing the gas through a strong solution of caustic potash to remove the hydrogen cyanide and then over wood charcoal to remove the carbon bisulphide. The gas was dried by being passed over calcium chloride, and then solidified at liquid air temperature. All permanent gases were pumped out of the U-tube containing the solid COS by means of a mercury pump. The liquid air was then replaced by a mixture of solid CO₂ and alcohol at -80° C., when it was observed that the vapour pressure of the liquid COS was about 30 cm. of mercury. The CO₂ mixture was then removed and samples of the gas collected over mercury. It was further purified before being introduced into the viscometer by fractional distillation at liquid air temperature. The liquid air having been replaced by CO₂ and alcohol at -80° C., it was possible on account of the comparatively high vapour pressure of COS at this temperature to pump off successive quantities of dry COS sufficient to fill the viscometer at atmospheric pressure.

Experimental Results. (Table I.)

We have $t_{15} = 69.96$ secs., and $t_{100} = 90.64$ secs.

The ratio of these times of fall gives the ratio of the viscosities at the corresponding temperatures.

Thus

$$\frac{\eta_{100}}{\eta_{15}} = \frac{t_{100}}{t_{15}} = \frac{90.64}{69.96} = 1.2956.$$

* Moissan, *Traité de Chimie*, vol. ii. p. 318.

TABLE I.

Each time recorded is the mean of four observations in each direction for the whole pellet, and of three for the pellet when divided into two segments. The letters in parentheses indicate the order in which the observations were made.

Temp. (deg. C.).	Time of fall (secs.).		Capillary correction (x).	Corrected time (t).	Time at	
	Whole pellet.	Two segments.			15°0C.	100°0C.
(a) 15·29 ...	73·04	76·35	0·0416	70·01	69·92	—
(b) 15·44 ...	73·08	76·25	0·0399	70·16	70·05	—
(c) 15·63 ...	73·02	76·22	0·0403	70·07	69·91	—
				Mean	69·96	—
(c) 99·9 ...	91·51	92·43	0·0099	90·60	—	90·63
(d) 99·9 ...	91·54	92·48	0·0101	90·62	—	90·65
				Mean	—	90·64

Assuming Sutherland's law to hold for this gas, the value of Sutherland's constant obtained is $C = 330$.

Also at 15°·0 C.,

$$\frac{t_{\text{COS}}}{t_{\text{air}}} = \frac{69·96}{104·70} = 0·6682.$$

Correcting for difference of slipping of COS and air, we obtain

$$\frac{\eta_{\text{COS}}}{t_{\text{air}}} = 0·6668.$$

On the assumption that the viscosity of air at 15°·0 C. is $1·799 \times 10^{-4}$ C.G.S. units, the values for COS are

$$\eta_{15} = 1·200 \times 10^{-4} \text{ C.G.S. units}$$

and $\eta_{100} = 1·554 \times 10^{-4} \text{ C.G.S. units};$

and by extrapolation using Sutherland's formula,

$$\eta_0 = 1·135 \times 10^{-4} \text{ C.G.S. units.}$$

Calculation of Molecular Dimensions.

The particular dimension calculated from the above results is the mean area \bar{A} which the molecule presents in mutual collision with others. The basis of this calculation is Chapman's formula (*loc. cit.*) modified in its interpretation in the manner suggested by Rankine. The value obtained is $\bar{A} = 1·06 \times 10^{-15} \text{ cm.}^2$ which may be subject to an error of 2 or 3 per cent.

Summary of Results.

TABLE II.

Viscosity in C.G.S. units $\times 10^{-4}$.			Sutherland's constant.	Mean collision area. $\text{cm.}^2 \times 10^{-15}$.
15°·0 C.	100°·0 C.	0°·0 C.		
1·200	1·554	1·135	330	1·06

In conclusion the author gladly acknowledges the grant for this research, which was made by the Government Grant Committee of the Royal Society, and also wishes to thank Professor Rankine for his continued help and advice.

Imperial College of
Science and Technology, S.W. 7.
1st May, 1922.

XXVI. *On the Molecular Structure of Carbon Oxysulphide and Carbon Bisulphide.* By A. O. RANKINE, D.Sc.,
Professor of Physics in the Imperial College of Science and Technology.*

1. **T**HERE are at the present day in the process of development several theories of atomic and molecular structure which are in many respects discordant. They have, however, at least one feature of general agreement—namely, the common view that the atoms of the inert gases occupy unique positions in the various schemes. The distribution of the electrons with respect to the nuclei in these atoms is regarded as having the characteristic of *completeness*, so that there is displayed no marked tendency to lose electrons or to capture additional ones. Moreover, atoms other than those mentioned are believed to have in varying degrees what may be called deficiencies and redundancies of extra-nuclear electrons, which they endeavour to adjust by entering into suitable combinations with one another; so that either by the process of give and take, or by common use of the same electrons, configurations corresponding closely to those of the inert atoms are attained by the individual atoms forming the compound.

2. These views of chemical combination find their most

* Communicated by the Author.

complete expression in the theory of Lewis and Langmuir *, particularly in relation to the type of compound with which this paper is concerned—namely, that in which atoms, deficient in electrons, are regarded as sharing them in order to reach the completeness of inert configurations. The main purpose of this paper is to apply the principles of this theory to the special case of the molecule of carbon oxysulphide, and to show that the molecular dimensions of this compound, as derived from viscosity data, are consistent with the Lewis-Langmuir view of its constitution. This test of the validity of the theory is made possible by the recent measurements by C. J. Smith † of the viscous properties of the gas in question. Similar calculations for the molecule of carbon bisulphide have been made, and these await verification or otherwise when the necessary viscosity data are available.

3. Carbon oxysulphide belongs to a family of three compounds having the chemical constitutions CO_2 , COS , and CS_2 . The two former are gaseous at ordinary temperatures, and the latter a highly volatile liquid. In all of them carbon is a constituent, and COS can be regarded as the molecule obtained by the substitution of a sulphur atom for one of the oxygen atoms in CO_2 , or by the reverse substitution in CS_2 . It is probable that the carbon atom occupies the central position in each molecule, and that the nuclei of the three atoms lie in each case upon a straight line.

4. According to the Lewis-Langmuir theory (*loc. cit.*), the atoms in these molecules are linked together by sharing external electrons in such a manner that each atom approximates to the configuration of the inert atom at the end of the corresponding row in the periodic table. Thus, in CO_2 the central carbon atom shares altogether eight electrons, four on each side with an oxygen atom. The electron configuration thus formed is that of three neon atoms in a row, for the inert atom corresponding to both carbon and oxygen is neon. In the molecule COS there are again eight electrons shared by the carbon atom, four on one side with the oxygen atom, and four on the other side with the sulphur atom. The electron arrangement thus attained is that of two neon atoms (corresponding to the oxygen and carbon) and one argon atom (corresponding to the sulphur). Applying a similar argument to the CS_2 molecule, we are led to regard it as resembling closely the electron distribution of inert atoms in the sequence argon-neon-argon in a line. In other words, we can treat each carbon or oxygen atom in a

* I. Langmuir, Journ. Amer. Chem. Soc. vol. xli. p. 868.

† C. J. Smith, *suprà*, p. 289.

molecule as having nearly the same dimensions as a neon atom, and each sulphur atom in combination as approximating to the dimensions of an atom of argon.

5. The remaining question of how far apart are the nuclei of the atoms in the molecule finds a satisfactory answer in the work of W. L. Bragg*, whose X-ray crystal measurements have enabled him to assign probable values for the radii of the outer electron shells of the atoms of the inert gases. The only values with which we are at the moment concerned are those of neon and argon, which are given respectively as 0.65 and 1.03 Ångström units. In cases like those under consideration, where outer electrons are playing a double part, the sharing is equivalent to contiguity of the outer shells, so that the distance apart of the nuclei is the sum of the radii of the appropriate inert atom shells. Thus for CO₂, which is pictured as three neon atoms in line, the three nuclei are equally spaced and separated by distances equal to twice the radius of the neon outer shell, *i. e.* $2 \times 0.65 \text{ Å} = 1.30 \text{ Å}$. In COS the distance between the carbon and oxygen nuclei is the same, namely 1.30 Å, but the distance between the carbon and sulphur nuclei is the sum of the radii of the outer electron shells of the neon and argon atoms, *i. e.* $0.65 \text{ Å} + 1.03 \text{ Å} = 1.68 \text{ Å}$. The three nuclei in COS are thus unequally spaced on account of the greater size of the argon atom. In CS₂ the distance between the carbon nucleus and each sulphur nucleus is also 1.68 Å, and the three nuclei are again spaced symmetrically.

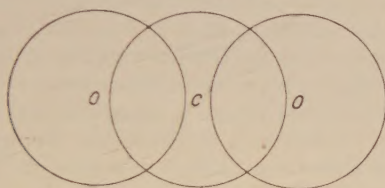
6. It is evident that none of the three molecules under consideration, if their configurations are as indicated, can be expected to display spherical symmetry. In these circumstances it is necessary to interpret in a special way the results of the well recognized method of calculating molecular dimensions from viscosity data. The quantity which is actually derivable from the formula is the mean value of the area which the molecule presents, for all possible orientations, as a target for mutual collision with other molecules in the gas. This area the author† has ventured to call the *mean collision area*, and its value for COS is given by C. J. Smith (*loc. cit.*) as $1.06 \times 10^{-15} \text{ cm.}^2$ The immediate problem before us is to find how nearly the tentative model of this molecule described above would exhibit this value for its mean collision area. The values of

* W. L. Bragg, Phil. Mag. vol. xl. p. 169.

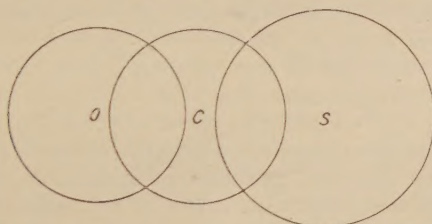
† A. O. Rankine, Proc. Roy. Soc. A, vol. xcvi. p. 360, and Proc. Phys. Soc. vol. xxxiii. p. 362.

the mean collision areas of the constituent configurations (which we are taking to be those of neon and argon) are known, and it is usual to regard these symmetrical inert atoms as behaving as elastic spheres for purposes of collision. The radii of these collision spheres, as we may call them for the sake of precision, are 1.15 \AA and 1.44 \AA respectively, and they are considerably larger than those of the corresponding outer electron shells, so that they overlap when

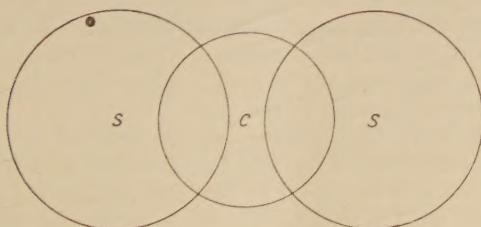
Fig. 1.—*Molecular Dimensions from the point of view of the Kinetic Theory.*



The Carbon Dioxide Molecule: equivalent to three linked atoms of Neon.



The Carbon Oxysulphide Molecule: equivalent to two Neon atoms and one Argon atom linked together.



The Carbon Bisulphide Molecule: equivalent to two Argon atoms linked together by one Neon atom.

the nuclei are separated by the distances demanded by electron sharing. Fig. 1 shows three models, drawn to scale, representing what we may conceive CO_2 , COS , and CS_2 to be like for purposes of intermolecular encounters. CO_2 may be regarded as three overlapping spheres, each of the neon

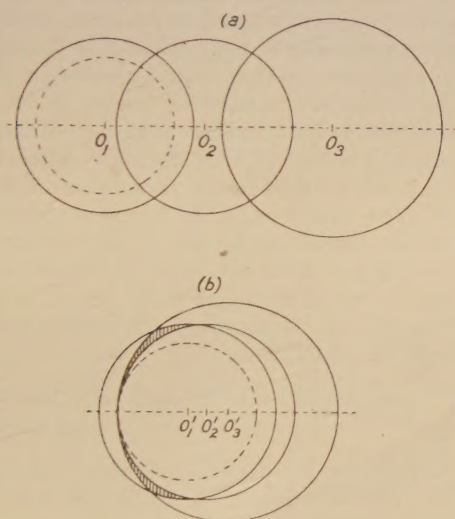
collision size, with centres separated by the distances already specified. In COS we take instead of one of the extreme neon spheres an argon collision sphere; while in CS₂ both the outer spheres are of the argon size. In all three cases the diagram represents all the nuclei in the plane of the paper, and the line joining them is evidently an axis of symmetry. If these symmetrical axes are variously oriented, the area presented by the model assumes different values, and our problem is to calculate the mean value of this projected area for comparison with that deduced from viscosity data. The author (*loc. cit.*) has already derived the necessary formulæ for this purpose, and has shown that the result obtained by application to the first model in fig. 1, namely CO₂, is very nearly equal to the actual mean collision area of the carbon dioxide molecule. In other words, a carbon dioxide molecule behaves in collision as though it had the configuration of three neon atoms in a straight line and with outer electron shells contiguous.

7. *Calculation for the COS Model.*—In the model which we are taking to represent the COS molecule, the calculation in the strictest sense is greatly complicated by reason of the particular distribution of the spheres. The exact formulæ which have been obtained (*loc. cit.*) for equal and unequal spheres only apply rigidly to cases where a special relation exists between the diameters of the spheres and the distances apart of their centres; and the model under consideration does not fulfil this condition. But by regarding the problem from two different points of view, we can obtain, by means of the comparatively simple formulæ already available, upper and lower limits which are so close together as to render unnecessary the laborious exact calculation. This course is all the more justifiable because it is fully recognized that the general treatment of the problem itself can only be taken as a first approximation to the truth.

8. Let us consider the effect on the area of projection of the model (reproduced in the full lines of fig. 2, *a*) caused by variations of orientation of the symmetrical axis joining the centres O₁, O₂, and O₃ of the constituent spheres. It will be convenient to speak of the sphere with centre O₁ simply as sphere 1, and so on, and of the projections of the spheres, which will of course be circles, as projection 1 etc. As the axis O₁ O₃ approaches the line of sight, the projections of the centres approach one another, and the eclipsing of the spheres becomes more and more marked. Up to a certain point the total projected area is equal to the sum

of the areas of the whole of projection 3, the crescent formed by the overlapping of projection 3 over projection 2, and the crescent formed similarly by the eclipse of projection 1 by projection 2. Before the eclipsing of 2 by 3 is complete, however, projection 3 begins to encroach upon regions of projection 1 which are not already covered by projection 2. It is this fact that introduces into the exact treatment of the problem the complications to which reference has already been made. Thus in fig. 2, *b*, which shows the projected area for that orientation of the axis for which the eclipse of 2 by 3 is just complete, the crescent formed by 2 and 1 still

Fig. 2.



survives, but parts of it (as indicated by the shading) are covered by projection 3. The projected centres are O_1' , O_2' , and O_3' respectively, and this particular state of affairs occurs when the angle between $O_1 O_3$ and the direction of projection is $9^\circ 47'$ for the spheres having the dimensions and distribution already specified.

9. Overlapping of the type just indicated, like all overlapping, has the effect of reducing the projected area; it is therefore clear that if we neglect it we shall obtain too large a value for the mean area of projection—that is, an upper limit will be obtained by taking the mean collision area as the sum of the three parts : (a) the area of the circle 3, (b) the mean value of the area of the crescent formed by circles 3 and 2 (c) the mean value of the area of the crescent

formed by circles 2 and 1. The first of these quantities is the area of the central cross-section of the argon sphere itself, viz. $0.648 \times 10^{-15} \text{ cm.}^2$; the two latter are readily obtained from the graph in the paper already mentioned*. They prove to be $0.217 \times 10^{-15} \text{ cm.}^2$ and $0.226 \times 10^{-15} \text{ cm.}^2$ respectively. The total is $1.09 \times 10^{-15} \text{ cm.}^2$, and this provides our upper limit.

10. With regard to the lower limit, we can obtain a satisfactory value by contemplating a variation of our model, which avoids the special type of overlapping responsible for complications. A suitable change for this purpose is to substitute for the sphere 1 a smaller sphere having the same centre but of such magnitude that its projection becomes just eclipsed by projection 2 at the same orientation of the symmetrical axis for which projection 2 is just eclipsed by projection 1, as shown by the dotted circles in fig. 2. The radius of the necessary sphere is found to be 0.93 \AA as compared with the original value 1.15 \AA . Examination of the projection of a sphere of this size, in relation to the other two projections, shows that for no orientation does eclipsing of the shaded type appear, and the formulæ already available enable the mean area of projection to be calculated exactly. The value so obtained will, however, obviously be less than the true value aimed at, on account of the reduction of size assumed for sphere 1. Using the graph already mentioned, the lower limit thus derived is

$$0.648 \times 10^{-15} \text{ cm.}^2 + 0.217 \times 10^{-15} \text{ cm.}^2 + 0.138 \times 10^{-15} \text{ cm.}^2 \\ = 1.00 \times 10^{-15} \text{ cm.}^2$$

11. The foregoing justifies the assertion that a molecular model having the dimensions of an argon atom succeeded by two neon atoms in line and spaced according to the demands of outer electron contiguity may be expected to have a mean collision area intermediate between

$$1.09 \times 10^{-15} \text{ cm.}^2 \\ \text{and} \quad 1.00 \times 10^{-15} \text{ cm.}^2$$

The actual value of the mean collision area of the COS molecule, as determined from viscosity is

$$1.06 \times 10^{-15} \text{ cm.}^2$$

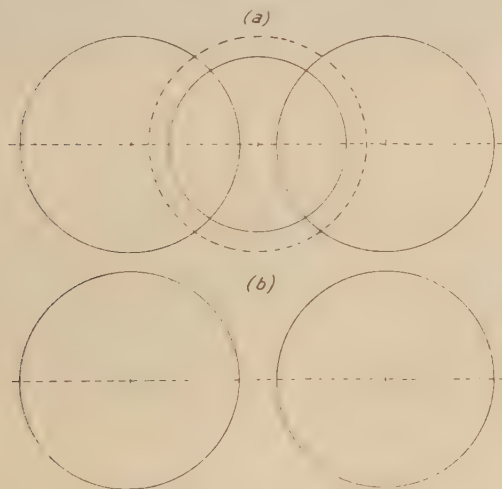
with a possible error of 2 or 3 per cent. It falls definitely between the upper and lower limits obtained from our calculations, and seems to provide striking corroboration of

* A. O. Rankine, Proc. Phys. Soc. vol. xxxiii. p. 371.

the theory upon which the estimates are based. But we must be content with the conservative remark that the dimensions of the carbon oxy sulphide molecule, as found by the application of the kinetic theory, are consistent within the limits of experimental accuracy with the view that the three atoms of the molecule, by sharing external electrons, assume the electron configurations and behaviour in collision of particular groupings of the neighbouring inert atoms.

12. *Calculation for the CS₂ Model.*—Although there exist at present no data for carbon bisulphide which suffice to calculate the mean collision area of the molecule in the gaseous state, the success of the previous comparison would appear to justify a prediction of its value by consideration of the appropriate model. This has been reproduced in the full lines of fig. 3. *a*. Here again the model is

Fig. 3.



one which does not lend itself to exact solution without laborious calculation; but again, also, we can obtain satisfactorily close upper and lower limits. The area of projection will clearly be less than that corresponding to the model in which the dotted sphere is substituted for the small central one, so that we have three equal spheres of the argon size in line: it will, on the other hand, be greater than if the central sphere is entirely dispensed with, so that there are two equal argon spheres only, as represented in fig. 3, *b*. The dimensions of the spheres and the distances

apart of their centres have already been stated; and both modified models have mean areas of projection which are very easily calculated. The upper limit thus determined proves to be 2.12 times the collision area of the argon atom; the lower limit is 1.90 times the same area. Using the known value 0.648×10^{-15} cm.² for the collision area of the argon atom, we find that the mean area of projection of the model consisting of two argon atoms with an intermediate neon lies between

$$1.37 \times 10^{-15} \text{ cm.}^2$$

$$\text{and } 1.23 \times 10^{-15} \text{ cm.}^2$$

We may venture to predict with some confidence that the mean collision area of the CS₂ molecule, when determined, will be found to be between the above values. A more exact estimate could of course be made, but the degree of accuracy at present attainable in determining molecular dimensions from viscosity measurements is not sufficient to render the additional calculation worth while.

Summary.

On the assumption of the validity of the Lewis-Langmuir view of molecular constitution, the probable behaviour during encounters has been examined for the molecules of carbon oxysulphide and carbon bisulphide. In the former case it is shown that the molecular dimensions as derived from the application of the kinetic theory to the viscosity measurements of C. J. Smith, are in striking accordance with the results of the above examination. In the latter case comparison is not yet possible, on account of the absence of necessary data.

Imperial College of Science and Technology,
May 11th, 1922.

XXVII. *The Rise of γ -Ray Activity of Radium Emanation.* By F. P. SLATER, *M.Sc. (Vict.), B.A. (Cantab.)*.*

IN a previous paper † it has been shown how the initial rise of γ -ray activity, starting from pure radium emanation, depended on the nature of the walls of the tube containing the gas, the reason being that a small but

* Communicated by Prof. Sir E. Rutherford, F.R.S.

† Slater, *Phil. Mag.* vol. xlii. p. 904 (1921).

detectable γ radiation was excited in the walls by the impact of the α particles emitted by the emanation. The amount of this excited radiation was, however, very small when the walls of the tube were composed of atoms of low atomic weight, and for a lining of pure paper the γ -ray activity of the emanation and its products was found to rise practically from zero. Under such conditions the γ radiations from the tube are due only to the products radium B and radium C.

Taking the number of emanation atoms disintegrating per second at initial time as unity, the number of radium-B atoms disintegrating per second at any subsequent time t is

$$\lambda_2 \lambda_3 \sum_{\lambda=1,2,3} \frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)},$$

where $\lambda_1, \lambda_2, \lambda_3$ are the transformation constants of the emanation and the products A, B, and C respectively. This quantity is tabulated for various times up to 220 minutes at the end of this paper (Table II.).

Similarly, the number of radium-C atoms disintegrating per second at time t is

$$\lambda_2 \lambda_3 \lambda_4 \sum_{\lambda=1,2,3,4} \frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)(\lambda_4 - \lambda_1)}.$$

Tables for this quantity for various times up to 258 minutes have been given by Moseley and Makower* and by Rutherford†.

The rise in γ -ray activity of a tube filled initially with pure emanation can therefore be represented by

$$\begin{aligned} K \lambda_2 \lambda_3 \sum_{\lambda=1,2,3} \frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} \\ + (1-K) \lambda_2 \lambda_3 \lambda_4 \sum_{\lambda=1,2,3,4} \frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)(\lambda_4 - \lambda_1)}, \end{aligned}$$

where K is the fraction of the ionization, measured under given absorption conditions, due to radium B when in radioactive equilibrium with radium C.

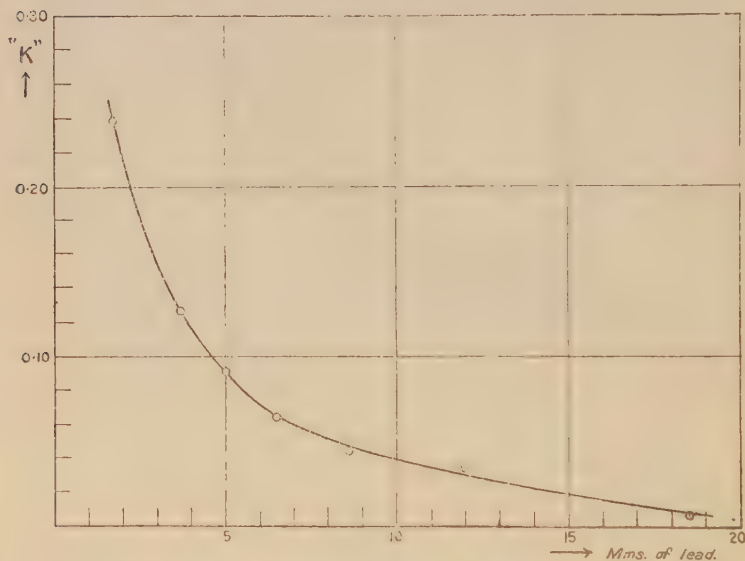
Thus it is necessary to determine " K ." Since the γ rays

* Moseley and Makower, *Phil. Mag.* vol. xxiii. p. 302 (1912).

† Rutherford, 'Radioactive Substances,' p. 499.

from radium B are less penetrating than those from radium C, "K" depends on the thickness of matter through which the radiations pass before entering the ionization chamber. Rise curves have been experimentally determined for different thicknesses of absorption material, both lead and aluminium being used. The values of K for various thicknesses have been deduced by trial, and are shown in fig. 1.

Fig. 1.



A comparison of the experimental and calculated rise curves of the γ -ray activity through 12.0 mm. of lead is given in fig. 2. After six minutes from the introduction of pure emanation, the calculated and experimental curves agree very closely.

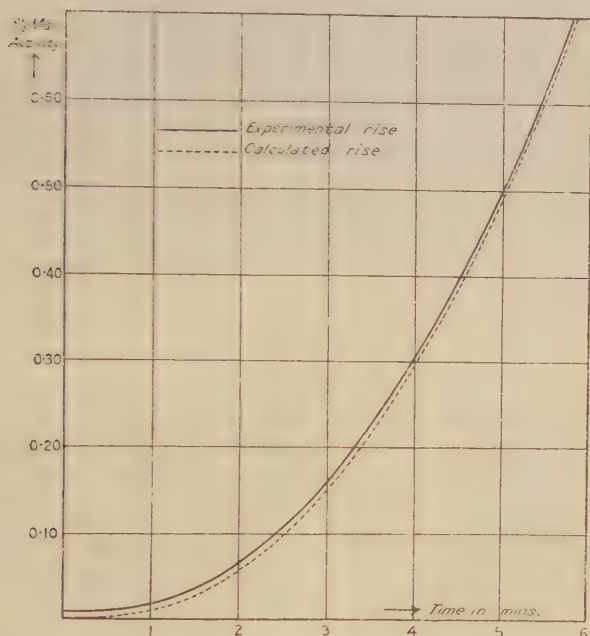
From these curves the absorption coefficient of the radium B- γ rays can be deduced, and the values found are given in Table I, along with comparative determinations by Makower and Moseley (*loc. cit.*) and Rutherford and Richardson*.

The values of the absorption coefficients for the thicknesses of aluminium are somewhat doubtful, since the supposition of homogeneity of the radium-C γ rays is not justifiable through such small thicknesses. The increasing

* Rutherford and Richardson, *Phil. Mag.* vol. xxv. p. 722 (1913).

value of μ (cm.^{-1}) with decreasing thickness of absorption material (see Table I.) is to be expected, since Rutherford and Richardson (*loc. cit.*) showed that radium B emits certainly two types of radiation having absorption coefficients in aluminium of 0.51 cm.^{-1} and 40.0 cm.^{-1} , and possibly a third type ($\mu=230.0^{-1}$ in aluminium).

Fig. 2.—Rise of γ activity from Radium emanation through 12.0 mm. of lead.



The absorption coefficients in lead only, given in Table I., are corrected for obliquity of the rays entering the electro-scope, and King's correction is used as given in Case II. of his paper*,

$$\frac{I_t}{I_0} = \frac{f(\mu t) - \cos \theta f[\mu t \sec \theta]}{1 - \cos \theta}.$$

where I_t and I_0 are the intensities of the radiation emerging through a plate of thickness t cm. and incident radiation respectively, μ the absorption coefficient expressed in cm.^{-1} , and θ the semi-angle of the cone of rays entering the electro-scope.

* King, *Phil. Mag.* vol. xxiii. p. 248 (1912).

TABLE I.

Absorbing medium is Lead, except where otherwise shown.

Thickness of Absorbing Plate.	Value of μ (cm. ⁻¹) for Radium-B rays.	Moseley and Makower.	Rutherford and Richardson.
16.0-20.0 mm.....	2.7 cm. ⁻¹	—	Varying from
10.0-15.0 „ ..	2.8 cm. ⁻¹	—	11.0 cm. ⁻¹
4.0- 6.0 „ ..	4.1 cm. ⁻¹	4.0 cm. ⁻¹ (lead).	to 2.8 cm. ⁻¹ in
1.5- 2.0 „ ..	6.2 cm. ⁻¹	6.0 cm. ⁻¹ (lead).	lead.
3.0- 4.0 „ (Aluminium).	1.7 cm. ⁻¹ (Al).		
0.75 mm. (Aluminium) ...	10.0 cm. ⁻¹ (Al) ?		

TABLE II.

Rise of Radium B from Radium Emanation.

Maximum = 0.97480 is taken as unity.

Time in mins.	Calculated rise of Radium B.	Time in mins.	Calculated rise of Radium B.	Time in mins.	Calculated rise of Radium B.
1	0.00269	14	0.2260	110	0.9502
2	0.01016	16	0.2649	120	0.9643
3	0.02129	18	0.3023	130	0.9750
4	0.03513	20	0.3379	140	0.9835
5	0.05115	30	0.4942	150	0.9886
6	0.06862	40	0.6135	160	0.9929
7	0.08718	50	0.7066	170	0.9956
8	0.10647	60	0.7780	180	0.9979
9	0.12622	70	0.8329	190	0.9992
10	0.14624	80	0.8748	200	0.9998
11	0.16637	90	0.9058	210	0.9999
12	0.18041	100	0.9315	214	1.0000
				220	0.9999

Summary.

Curves showing the rise of γ -ray activity from pure radium emanation measured through a wide range of absorption thickness of matter have been determined and utilized in deducing the absorption coefficients of the heterogeneous γ radiation from radium B.

My thanks are due to Professor Sir E. Rutherford for his invaluable help in carrying out this research, and to Mr. G. A. R. Crowe for the preparation of the radioactive material.

XXVIII. *An Experimental Test of Smoluchowski's Theory of the Kinetics of the Process of Coagulation.* By JNANENDRA NATH MUKHERJEE, D.Sc., Professor of Physical Chemistry, University of Calcutta, and B. CONSTANTINE PAPACONSTANTINOU, D.Sc., Assistant Professor of Chemistry, University of Athens*.

A short account of the Theory.

IN some experiments on the degree of dispersion of colloidal arsenious sulphide on the rate of coagulation, it has been shown (J. Amer. Chem. Soc. vol. xxxvii. p. 2026, 1915; and Sen, Trans. Chem. Soc. vol. cxv. pp. 467-8, 1919) that the finer sol is less stable. In 1915 one of us pointed out the obvious connexion with the increased facilities of coalescence. The smaller particles have a more vigorous Brownian movement due to the smaller frictional resistance of the medium. This would be clear from the well-known equation of Einstein. The diminution in the mean distance between the particles also increases the rate of collisions. It was stated that the adsorption theory does not take these factors into consideration. Recently Smoluchowski (*Zeit. Phys. Chem.* vol. xcii. p. 129, 1917) has been able to formulate the progress of the coalescence with time. His attention was drawn to the subject by Zsigmondy. Bredig (*Anorganische Fermente*, 1901, p. 15) suggested as the cause of coalescence an increase in surface tension with a decrease in the electric density on the particles. Zsigmondy (*Zeitsch. Physikal. Chem.* vol. xcii. p. 500, 1918) modified this idea in the sense that there is an attraction between the particles which increases with decrease in the electric charge. As a result of this attraction he assumes that when one particle comes within a certain distance of another, the two coalesce. This distance is taken as a measure of the force of attraction and is called the radius of the sphere of action. It has been shown by Zsigmondy that the time required for a definite colour-change in a gold sol gradually decreases with rise in electrolyte concentration till it reaches a minimum †, which does not change any further with higher

* Communicated by Prof. F. G. Donnan, F.R.S.

† Similar minimum times have been observed with cupric sulphide and mercuric sulphide sols by the writers. A copper sulphide sol gave two minutes as the time necessary for the appearance of visible clots when the concentration of the precipitating electrolyte (barium chloride) was varied from N/300 to N/20. At dilutions higher than N/300 the time was observed to increase as usual (Mukherjee and Sen, *loc. cit.*).

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concentrations. This was assumed to prove that the radius of attraction reached a maximum value.

Smoluchowski utilized this idea of a sphere of action to avoid a consideration of the forces that influence the coalescence. He considers the probability of particles coming within their mutual sphere of action when the radius of the sphere has a constant value determined by the conditions. It is assumed that as soon as a particle comes within the sphere of attraction by virtue of its Brownian movement the two particles coalesce. This discontinuous view of the obviously continuous process of coalescence was assumed to avoid a consideration of the nature and distribution of the forces that are present.

Considering the effect of the motion of each particle and also that each of the aggregates acts as a condensation centre, he derives the following equations :

$$\Sigma n = \frac{n_0}{1 + \frac{t}{T}}, \quad \dots \dots \dots (1)$$

$$n_1 = \frac{n_0}{\left(1 + \frac{t}{T}\right)^2}, \quad \dots \dots \dots (2)$$

$$n_k = n_0 \frac{(\alpha \cdot n_0 \cdot t)^{k-1}}{(1 + \alpha \cdot n_0 \cdot t)^{k+1}}, \quad \dots \dots \dots (3)$$

where " n_0 " denotes the total number of particles originally present per unit volume before coalescence begins. They are all assumed to be spherical and equal in size. " t " is the time in seconds that has elapsed since the electrolyte and the sol have been mixed. " T " is a constant characteristic of the rate of coagulation and is given by

$$T = \frac{1}{4 \cdot \pi \cdot D \cdot R_a \cdot n_0}, \quad \dots \dots \dots (4)$$

where " D "* is the diffusion constant as given by Einstein's equation ; $\alpha = 4 \cdot \pi \cdot D \cdot R_a$, and R_a is the radius of the sphere of action.

* $D = \frac{\Pi \cdot \theta}{N_0} \cdot \frac{1}{6\pi \cdot \eta \cdot r}$, where Π = the gas constant,
 θ = the absolute temperature,
 N_0 = Avogadro's number,
 η = the viscosity,
 and r = radius of the particle.

Σn denotes the total number of particles in all stages of coalescence in unit volume when the time is " t "; n_1 denotes the number of the primary particles whose original number was n_0 at the time " t "; n_k denotes the number of particles of the k th stage of coalescence—that is, the number of aggregates each of which consists of " k " of the primary particles. " k " is evidently an integer. In 1918 Zsigmondy published the results of an investigation to test this theory. He restricted his investigation to the rate of decrease in the primary particles (green in the ultramicroscope) in a colloidal gold sol when the minimum time of coagulation has been reached. He found that $Ra = 2.2$ times r , the radius of the particles. Similar values were obtained by Westgren and Reitstötter (*Zeitschr. Phys. Chem.* vol. xcii. p. 600, 1918) with more coarsely dispersed gold sols. The value of Ra/r , however, varied in one experiment from 1.4 to 3.8. The recent experiments of Kruyt and Van Arkel (*Rec. Trav. Chim. Pays-Bas*, vol. xxxix. [4] p. 656, vol. xl. p. 169, 1920) show greater variations. They are of opinion that there is some regularity in these variations. They could not observe a maximum value of $Ra \cdot r$ equal to 2. They found a maximum value equal to 0.73.

Smoluchowski, assuming from the data of Zsigmondy available at that time that $Ra/r = 2$, points out that the maximum rate of coagulation is reached when each collision between two particles is successful in bringing about a coalescence. When the rate of coagulation is slower, all the collisions are not successful in bringing about a coalescence of the particles. If " ϵ " is the fraction of the collisions that are successful in bringing about coalescence, then " T " in equations (1) and (2) takes the form

$$T = \frac{3}{4} \frac{N_0 \cdot \eta}{R_1 \cdot n_0 \cdot \theta \cdot \epsilon}, \quad \dots \dots \dots (5)$$

where N_0 , R_1 , n_0 , θ , and η have the same meaning as in equations (1) and (2).

Putting

$$\frac{3}{4} \frac{N_0 \cdot \eta}{R_1 \cdot \theta \cdot n_0} = \frac{1}{\beta}, \quad \dots \dots \dots (6)$$

we have

$$\Sigma n = \frac{n_0}{1 + T} = \frac{n_0}{1 + \beta \cdot \epsilon \cdot t} \quad \dots \dots \dots (7)$$

Since only " ϵ " is variable, a comparison of the coagulation time " t " for the same change in the sol makes it possible to determine the variation in the percentage of successful collisions and its dependence on the conditions of experiment. When the maximum rate is reached, $\epsilon=1$ and hence a measure of the absolute value of ϵ is possible.

Problems awaiting solution.—A glance through the experimental work would show that the assumption of the constancy of " T " is not well justified. The simplicity of Smoluchowski's equations consist in that there is only one constant. The experimental limitations are great, and it is quite possible that the discrepancies are due to the defects of the ultra-microscopic method. The other possibility is that the simplifying assumptions of Smoluchowski—for example, the constancy of " T " independent of the stage of coalescence—are not true within narrow limits. It is of great interest to know the limits within which these equations are valid.

The important questions that await solution in this connexion are :

- (a) the limits within which the above equations are valid ; and
- (b) if the above equations are valid, the variation of ϵ with concentration of electrolyte ;
- (c) the dependence of ϵ on the electric charge ;
- (d) the variation of ϵ with temperature.

In the following an account of an attempt to examine these factors, with the exception of (c), is recorded.

Indirect Methods.—Variations in physical properties that occur simultaneously with the process of coagulation can be utilized to measure the rate of coalescence.

Smoluchowski pointed out that the viscosity measurements of Gann (*Koll. Chem. Beihefte*, vol. viii. p. 67 (1916)) do not satisfy the main requirements of his equations—namely, a similarity in the form of the curves (showing the variation in viscosity with time) independent of the nature of the electrolyte. He concludes that viscosity changes do not form a measure of the coagulation process. Yet he considers that the method is suitable for a quantitative comparison of the effect of various concentrations on the values of ϵ when the curves are similar.

The variation in physical properties, however, is likely

to show the validity of the fundamental equations of Smoluchowski. The fact that the curves showing the change in viscosity with time are dissimilar shows that these assumptions are not justified, and Smoluchowski thinks that " T " is dependent on the magnitude of the aggregates.

Since as yet it is not possible to express physical properties—*e. g.*, the viscosity or the absorption of light—in terms of definite functions of the number and size of particles, a quantitative comparison of different sols is not possible by indirect methods. We have, therefore, to restrict ourselves to the same sol.

Experiments with Gold Sols.—An examination of the changes in the colour of gold sols on the addition of an electrolyte showed (Mukherjee and Papaconstantinou, Trans. Chem. Soc. vol. cxvii. p. 1563 (1920)) that the variation in the absorption of light of gold sols affords an easy and accurate method suitable for this purpose. The gold sols prepared by the nucleus method of Zsigmondy conform very nearly to the requirements of equations (1) to (3) in so far as the particles are fairly uniform in size. It would be very convenient to work with a sol with reproducible properties, as data obtained on different dates with different preparations could be rigorously compared.

It was found that a sol on standing for some time undergoes somewhat irregular changes, which may in part be due to dust particles getting in accidentally. In spite of all precautions, one cannot be sure that there is no such variation in a particular sample. This variation is not wholly due to the fungus that grows in these sols. For this reason it is necessary to vary one factor only at a time and compare its effects.

The comparison was therefore restricted to the same sol so long as it showed no variation in its properties.

The Constancy of " T " in Equations (1) to (3) during the Process of Coalescence.

According to the simple assumptions of Smoluchowski, the progress of coalescence should be uniformly the same for various electrolytes and for their different concentrations. The constancy of " T " implies that if we assume a series of consecutive stages of coalescence of a sol—under a definite set of conditions, namely a definite electrolyte concentration

and temperature—following each other by intervals of time equal to “ δt ,” they are each characterized by a definite number and manner of distribution of particles of each category (primary, secondary, etc.). Let us indicate the stage of coalescence corresponding to the time “ t ” seconds (since the sol and the electrolyte were mixed) under the given conditions by the numbers

$$\Sigma N, N_1, N_2, N_3, \dots N_k \dots,$$

where the subscripts refer to the number of primary particles by the union of which the aggregate is composed. Thus N_k denotes the number of aggregates, each of which is composed of “ k ” primary particles. “ k ” is evidently an integer.

Similarly let us denote the stage of coalescence corresponding to the time t' ($=t + \Delta t$) by

$$\Sigma N', N_1', N_2', N_3', \dots N_k' \dots$$

These stages of coalescence are independent of external conditions so long as equations (1) to (3) are valid. The only change that external conditions can bring about is a variation in the value of T —that is, if the external conditions are varied the sol will always pass through the same consecutive stages of coalescence and only the rapidity of succession of these stages will be determined by them. Any property which varies continuously with the progress of coalescence without having any maxima or minima can be utilized to characterize the stages of coalescence; for each value of this property is characteristic of the time that has passed since the mixing of electrolyte and sol. According to the equations of Smoluchowski, the times taken to reach any particular stage depend only on the value of “ T ,” which is constant under a definite set of conditions. Let us compare two different electrolytes, A and B, of concentrations C_1 and C_2 . Let us suppose that after the time “ t ” the stage of coalescence indicated by

$$\Sigma N, N_1, N_2, N_3, \dots N_k \dots$$

has been reached when the electrolyte is “A” of concentration C_1 . This stage of coalescence has a definite value for the physical property we are considering, and is independent of the value of T . Let us assume that “ T_1 ” and “ T_2 ” are the corresponding values of “ T ” for the two cases. To be definite, we shall consider the variation in the

total number of particles of all categories, which varies continually with the progress of coalescence. Let us assume that at the times " t_1 " and " t_2 " both electrolytes have reached a state at which the total number of particles is the same. From equation (1) we have, therefore,

$$\Sigma n = \frac{n_0}{1 + \frac{t_1}{T_1}} = \frac{n_0}{1 + \frac{t_2}{T_2}} \dots \dots \dots (8)$$

or

$$\frac{t_1}{T_1} = \frac{t_2}{T_2} \dots \dots \dots (9)$$

The general equation (3) may be written as

$$n = \frac{n_0 \cdot \left(\frac{t}{T}\right)^{k-1}}{\left(1 + \frac{t}{T}\right)^{k+1}} \dots \dots \dots (10)$$

Since n_0 and k are constants, if $\frac{t}{T}$ is constant, n_k has a

fixed value—that is, the condition $\frac{t_1}{T_1} = \frac{t_2}{T_2}$, which is deduced

from the condition that Σn has a fixed value, also implies that the values of $n_1, n_2, n_3, \dots n_k$ are the same in both cases. This means, in other words, that a definite value of Σn fixes unequivocally the stage of coalescence. Therefore, from the deduction that the successive stages of coalescence are always the same and depend only on the time, any property of the sol that varies continuously can be utilized to represent a fixed value of Σn or n_1 or a definite stage of coalescence. A definite value of this property is thus characteristic of the stage of coalescence. It also follows from the above considerations that all curves showing a variation of this property with time should be similar. A deviation from this similarity, in itself, would mean that equations (1) to (3) do not represent the facts.

The absorption coefficients of gold sols for different wavelengths change on addition of an electrolyte in a complex manner. The theories of the colour of these sols as advanced by Maxwell Garnett (*Phil. Trans.* vol. cciii. A, p. 385, 1904; vol. ccv. A, p. 237, 1906) and by Mie (*Ann. der Phys.* [4] vol. xxv. p. 377) would lead one to expect that any change in the number and manner of

distribution of the particles n_1 , n_2 , etc. will produce a great change in the optical properties of the sol. This is in agreement with observations. Now, if the successive stages of coalescence were independent of the nature and concentration of the electrolyte, then the manner of variation of the complex absorption would be the same in each case. The absorption in the red region of the spectrum varies continuously, corresponding to each value of the absorption coefficient for a particular wave-length in this region; the values in the other parts should be fixed. If the contrary holds good, then the conclusion is obvious that the successive stages of coalescence are not independent of the nature and concentration of the electrolyte as assumed by Smoluchowski.

It has been found that for the stage indicated by the value of the coefficient of absorption for $683\ \mu\mu = 0.4985$, the values of the coefficient for the other wave-lengths given in the following table in column II. are independent of the nature of the electrolyte.

The concentrations of the electrolytes were such as to produce rapid coagulation. In columns III. and IV. the coefficients of the "nucleus sol" have been given for the original sol and for the stage of coagulation characterized by the value of the coefficient for $683\ \mu\mu = 0.4156$ (Mukherjee and Papaconstantinou, *loc. cit.*).

TABLE I.

Wave-length, in $\mu\mu$.	Absorption coefficients (k).			
	I.	II.	III.	IV.
683	0.0453	0.4985	0.0376	0.4156
602	0.1055	0.3679	0.1131	0.409
583	0.1518	0.3388	0.1595	0.3986
563	0.2076	0.3294	0.2076	0.336
547	0.2512	0.3238	0.2867	0.3732
523	0.3780	0.3780	0.3780	0.3882
506	0.4647	0.3581	0.3882	0.3780
475	0.3581	0.3198	0.3581	0.3780

*Comparison of the Values of "T" as a Test of
Smoluchowski's Theory.*

Since the absorption coefficient in the red region varies continuously with the coagulation and its magnitude is

sufficiently great, a definite value of the absorption coefficient for a fixed wave-length ($683\ \mu\mu$) can be taken as representing a definite stage of the coalescence.

In the following tables the absorption coefficients at different times are given for the wave-length $683\ \mu\mu$. The tables are taken from the paper by Mukherjee and Papaconstantinou, *loc. cit.*

TABLE II.

Electrolyte: Potassium Chloride.

Time in minutes, after mixing equal volumes of electrolytes and sol.	Absorption coefficients for various concentrations.		
	N/24.	N/26.	N/28.
—	0.0453	0.0453	0.0453
0.5	0.3732	0.2867	0.1683
1	0.438	0.3630	0.2257
1.5	0.4497	0.4046	—
2	—	0.438	0.2777
3	—	0.4497	0.3431
5	—	—	0.3836
9	—	—	0.4263
13	—	—	0.438
15	—	—	0.4497

TABLE III.

Potassium Nitrate.

Times.	Concentrations.		
	N/24.	N/26.	N/30.
—	0.0453	0.0453	0.0453
0.5	0.3336	—	—
1	0.4263	0.2866	0.269
1.5	0.4497	0.3271	0.3143
2	—	0.3629	0.3336
3	—	0.4156	0.3732
4	—	0.438	0.394
5	—	0.4497	—
8	—	—	0.4263
10	—	—	0.438
16	—	—	0.4497

TABLE IV.
Barium Chloride.

Times.	Concentrations.		
	0.852N/900.	0.852N/1000.	0.852N/1100.
—	0.0453	0.0453	0.0453
1	0.2257	—	0.1603
2	0.2867	—	0.2007
4	0.3529	—	0.2687
5	0.3836	0.3051	0.3051
7	0.438	0.3431	0.3237
8	0.4497	—	0.3336
9	0.4497	0.3836	0.3529
11	—	0.4263	0.363
13	—	0.4497	0.363
16	—	—	0.3732

The limits within which the rate of coalescence could be varied were restricted by the fact that when the rate is slow the particles begin to settle, leaving a clear layer at the top, and the measurements are not reliable. Also, with time, some of the particles stick to the sides of the vessel. Lastly, it is difficult to avoid dust particles for a long time.

The values given in Tables II.—V. were plotted graphically, and the time intervals given in Tables V.—VII. below were determined from these curves.

Each of these curves is characterized by a definite value of T (or ϵ). Corresponding to the three concentrations of any one of these electrolytes, there are three intervals which must pass in order that the absorption coefficient may have the same value. These intervals are co-related by the following relation according to equations (1) to (3) or (6) :—

$$\frac{t_1}{T_1} = \frac{t_2}{T_2} = \frac{t_3}{T_3}, \quad \dots \quad (11)$$

or

$$t_1 : t_2 : t_3 = T_1 : T_2 : T_3 = \frac{1}{\epsilon_1} : \frac{1}{\epsilon_2} : \frac{1}{\epsilon_3}. \quad \dots \quad (12)$$

Since T_1 , T_2 , and T_3 are constant, the ratio of the time-parameters corresponding to the same absorption coefficient should be independent of the absolute value of the absorption coefficient. Corresponding to different values of the absorption coefficient we get different values of t_1 , t_2 , and t_3 . All these values should show a constant ratio. In the

following three tables this comparison is made for the three electrolytes mentioned in Tables II.-IV.

TABLE V.
Electrolyte : Potassium Chloride.

Values of absorption coefficient.	Time in seconds.			Ratios.
	N/24.	N/26.	N/28.	
	t_1 .	t_2 .	t_3 .	$T_1 : T_2 : T_3$.
0.370	27	65	255	1 : 2.47 : 9.44
0.400	35-40	85	345	1 : 2.3 : 9.3
0.438	60	120	780	1 : 2.0 : 13.0
0.445	75	180	900	1 : 2.4 : 12.0
	Average.....			1 : 2.3 : 11.4
	Extreme deviation from average			7.4 % 19 %

TABLE VI.
Electrolyte : Potassium Nitrate.

Absorption coefficients.	Times.			Ratios.
	N/24.	N/26.	N/28.	
	t_1 .	t_2 .	t_3 .	$T_1 : T_2 : T_3$.
0.350	25 } 27	105	145	1 : 3.9 : 5.4
	30 }			
0.400	45	165	255	1 : 3.7 : 5.7
0.425	60	210	375	1 : 3.5 : 6.2
0.445	90	300	780	1 : 3.3 : 8.6
	Average			1 : 3.6 : 6.3
	Extreme variation from average			8.8 % 33 %

TABLE VII.
Electrolyte : Barium Chloride.

Absorption coefficients.	Times.			Ratios.
	N/24.	N/26.	N/28.	
	t_1 .	t_2 .	t_3 .	$T_1 : T_2 : T_3$.
0.300	135	277	345	1 : 2 : 2.55
0.327	165	345	430	1 : 2.1 : 2.6
0.350	225	430	540	1 : 1.91 : 2.4
0.370	265	480	780	1 : 1.81 : 3.0
	Average			1 : 1.93 : 2.64
	Extreme variation from average			6 % 13 %

It will be seen from Tables V. to VII. that the agreement is as good as can be expected. The variation in T is as great as 11 times, but the ratios are constant. The agreement

shows that the ratios of the values of T are independent of the time or the stage of coalescence. The ultramicroscopic measurements so far made show even during one experiment a much greater variation in T , as will be evident from the following tables :—

TABLE VIII. (a).
(Observer : Zsigmondy.)

Values of $\beta' = \frac{1}{T}$.

Series D.	Series E.	Series F.
0.083	0.105	0.040
0.028	0.058	0.0195
0.0302	0.049	0.0183
0.0309	0.0475	0.0153
—	0.0403	0.0187
—	—	0.0126

Zsigmondy used high concentrations of electrolyte for securing a rapid rate. When the rate of coagulation is slow and the duration of experiment is greater than a few minutes, he found that impossible values of β' are obtained. He thinks that the presence of impurities in the water used in diluting the sol for ultramicroscopic observations is the cause of this irregularity. In his case the maximum time covered by the experiments is 80 secs. Similarly, Westgren and Reitstötter, working with coarse gold sols, find the following range of variation in the constant :—

TABLE VIII. (b).
(Observers : Westgren and Reitstötter.)

Values of $\frac{Ra}{r}$.

	Series I.	Series II.	Series III.	Series IV.
	3.74	2.56	2.75	3.41
	2.47	2.81	2.60	2.80
	2.07	2.33	2.17	2.60
	2.10	2.31	2.40	2.48
	2.09	2.31	2.12	2.14
	1.62	—	—	—
	1.41	2.16	2.15	2.15
	—	2.19	—	2.05
Average	2.2	2.38	2.36	2.19
Extreme variation...	75 %	10 %	17 %	55 %

Kruyt and Arkel *, working with selenium sol and very slow rate of coagulation, find extremely wide variations in T in the same experiment.

TABLE IX.

(Observers : Kruyt and Arkel.)

Values of T (in hours).

I.	II.	III.	IV.
2.8	260	131	1.3
5.1	390	55	3.4
44	270	52	2.2
(43)	320	54	4.3
(157)	600	68	10.5
200	370	55	40
—	510	—	—
—	440	48	37
—	—	—	52
—	—	—	38

The above few instances will suffice to show the range of variations in " T " during the course of one experiment that has been observed in the ultramicroscopic measurements.

Considering that in Tables V. to VII. the ratios between the different values of T are taken, the range of variation is extremely small. *The actual deviations in the value of T in any one experiment must be much less than the extreme variations given.* This comparison leaves no room for doubt that " T " is a constant in the case of gold sols and within the limits of the rate of coagulation that have been studied. In fact, these data constitute the best evidence so far recorded in favour of the theory of Smoluchowski.

The Dependence of ϵ on the Concentration.

Tables V. to VII. show clearly how rapidly ϵ , the percentage of successful collisions, increases with concentration. A change of concentration in the ratio 24 to 28 increases the rate in the ratio 1:11 or 1:6 as the case may be. It would be extremely interesting to work with a sol which is less susceptible to impurities than these gold sols.

* *Rec. Trav. Chim. Pays-Bas*, vol. xxxix. [4] p. 656 (1920); [4] vol. xl. p. 169 (1921).

Variation of T or ϵ with Temperature.

Similarly, by determining the times required to produce a definite change in the colour of the sol for the same electrolyte concentration but different temperatures, we can determine the variation in ϵ with temperature.

From equation (3),

$$\Sigma n = \frac{n_0}{1 + \beta \cdot \epsilon \cdot t},$$

we get

$$\frac{n_0}{\Sigma n} = 1 + \beta \cdot \epsilon \cdot t. \quad . \quad . \quad . \quad (13)$$

Since a definite change of colour is being used, $\frac{n_0}{\Sigma n}$ is constant, or

$$1 + \beta \cdot \epsilon \cdot t = k_1, \text{ a constant.} \quad . \quad . \quad . \quad (14)$$

Substituting the value of β in (14), we get

$$1 + \frac{4}{3} \frac{Ra \cdot \theta \cdot n_0}{N_0 \cdot \eta} \cdot \epsilon \cdot t = k_1. \quad . \quad . \quad . \quad (15)$$

Since Ra , N_0 , and n_0 are constants, we have

$$\frac{t \cdot \theta \cdot \epsilon}{\eta} = k', \text{ a constant.} \quad . \quad . \quad . \quad (16)$$

The viscosity of colloidal gold solutions has been found to be practically equal to that of water, and the variation with temperature can be assumed to be equal to that of water. For different temperatures we have

$$\frac{t_1 \cdot \theta_1 \cdot \epsilon_1}{\eta_1} = \frac{t_2 \cdot \theta_2 \cdot \epsilon_2}{\eta_2}. \quad . \quad . \quad . \quad (17)$$

Since t_1 is experimentally determined and θ and η are known, variations in ϵ can be compared.

The experimental data are given below. They are taken from the same paper (pp. 1570-71).

TABLE X.

Electrolyte.	Standards*.	Temperatures.		
		15°.	30°.	50°.
N/30 Potassium chloride ..	V Sol. C.	5 min.	10 min.	8 min. 30 sec.
N/30 Potassium sulphate .	„ „ D.	30 sec.	10 sec.	10 sec.
N/30 Potassium nitrate ..	„ „ D.	42 „	18 „	12 „

* These refer to the protected gold sols used as standards for comparison of colour. See *loc. cit.*

TABLE XI.

Electrolyte: Barium Chloride. Sol. E.

Con- centrations. Standards.		Temperatures.			
		15°.	30°.	40°.	50°.
0.852 N/1000	V ₂	7 min.	6 min.	4 min. 50 sec.	4 min. 20 sec.
0.852 N/1000	B ₂	34 "	23 "	—	13 " 30 "
0.852 N/1200	V ₂	23 "	13 "	12 min. 30 sec.	6 " 15 "
0.852 N/1200	B ₂	124 "	74 "	62 min.	—

TABLE XII.

Electrolyte: Strontium Nitrate. Sol. F.

Con- centrations. Standards.		Temperatures.		
		15°.	30°.	50°.
N/1000	V ₃	1 min. 10 sec.	20 sec.	8 sec.
N/1000	B ₃	8 " 15 "	1 min. 40 sec.	45 "

At 15°, 30°, 40°, and 50°, η/θ has the values 3.96×10^{-5} , 3.31×10^{-5} , 2.1×10^{-5} , and 1.7×10^{-5} respectively. The values for the viscosity are taken from the tables in Kaye and Laby's book on Physical and Chemical Constants, p. 30, 1919.

From equation (17) we have

$$\epsilon_{15^\circ} : \epsilon_{30^\circ} : \epsilon_{40^\circ} : \epsilon_{50^\circ} \\ = (\eta/t\theta)_{15^\circ} : (\eta/t\theta)_{30^\circ} : (\eta/t\theta)_{40^\circ} : (\eta/t\theta)_{50^\circ}.$$

TABLE XIII.

Electrolyte.		Temperatures.		
		15°.	30°.	50°.
N/30 KCl	N/t $\theta \times 10^7$	1.32	0.50	0.33
N/30 K ₂ SO ₄	"	13.2	33	17
N/30 KNO ₃	"	9.43	18.4	14.0

TABLE XIV.

Electrolyte: Barium Chloride.

Con- centrations. Standards.			Temperatures.			
			15°.	30°.	40°.	50°.
0.852 N/1000	V ₂	$\eta/t\theta \times 10^8$	9.43	9.2	7.24	6.54
"	B ₂	"	1.94	2.4	—	2.1
Ratio between	{	V ₂	100	: 98	: 77	: 70
$\eta/t\theta$		B ₂	100	: 123	: —	: 108
0.852 N/1200	V ₂	$\eta/t\theta \times 10^8$	2.87	4.24	2.8	4.5
"	B ₂	"	53.22	74.5	64	—
Ratio between	{	V ₂	100	: 148	: 98	: 158
$\eta/t\theta$		B ₂	100	: 140	: 106	: —

TABLE XV.

Electrolyte : Strontium Nitrate.

Concentrations. Standards.			Temperatures.		
			15°.	30°.	50°.
N/1000	V ₃	$\eta/t\theta \times 10^6$	·565	1·65	2·1
„	B ₃	$\eta/t\theta \times 10^7$	·80	3·3	3·77
Ratio between {	V ₃	100	: 291	: 371
$\eta/t\theta$	B ₃	100	: 416	: 430

Since $\eta = t\theta$ is a constant for a definite electrolyte concentration and temperature according to Smoluchowski's equation, the ratios should be independent of the standard used. This is true within the limits of experimental error with ·852 N/1200 Barium Chloride. In the other two cases the variations are not great considering that we are comparing the ratios. A slight variation in each value will be magnified in the ratio. Taking into account the probable experimental error, it can be said that ϵ is roughly constant in each experiment.

On the other hand, the variation in ϵ with temperature is considerable. We have already seen that the irregularity in the variation of ϵ means that the precipitating power of the ions changes with the temperature (Mukherjee, *Trans. Chem. Soc.* vol. cxvii. p. 358, 1920).

Further experiments with arsenious sulphide are in progress on similar lines.

Summary.

(1) It has been shown that the equations of Smoluchowski on the rate of coalescence of the particles of gold sols agree with the results obtained by the writers.

(2) It has been suggested that the disagreement of the ultramicroscopic measurements with this theory may in part be due to the difficulties inherent in them.

Our best thanks are due to Professor F. G. Donnan for his kind interest and encouragement, and also to our friend, Professor J. C. Ghosh.

Physical Chemistry Department,
University College, London.

XXIX. *The Adsorption of Ions.* By JNANENDRA NATH MUKHERJEE, D.Sc., Professor of Physical Chemistry in the University of Calcutta*.

IN a paper in the Transactions of the Faraday Society (Far. Soc. Disc. Oct. 1921) an attempt has been made to define the nature of the adsorption of ions to which the origin and the neutralization of the charge of a colloidal particle are due. The origin of the charge was assumed to be due to the adsorption of ions by the atoms in the surface as a result of their chemical affinity.

It was pointed out that the adsorption of one kind of ions will impart a charge to the surface, in virtue of which ions of opposite sign will be drawn near the surface. In the liquid there remains an equivalent amount of ions of opposite sign. The electrical energy will be a minimum when these ions are held near the surface so that the distance between the oppositely charged ions has the minimum value possible under the conditions, and they will be held opposite to the ions chemically adsorbed. An "ion" so held will not be "free" to move if its kinetic energy is less than "W" the energy required to separate the ion from the oppositely charged surface. The number of such "bound" ions determines the diminution in the charge of the surface. When the concentration of ions of opposite charge in the liquid is small the number of ions "held" to the surface by electrical attraction will be small.

If the chemically adsorbed ions have a valency equal to " N_1 ," and if " N_2 " is the valency of the oppositely charged ions in the liquid in contact with the surface, then

$$W = \frac{N_1 \cdot N_2 \cdot E^2}{D \cdot x}, \quad (1)$$

where E = the electronic charge, x = the distance between the centres of the ions at the position of minimum distance, and " D " is the dielectric constant of water.

Depending on the concentration of the oppositely charged ions in the liquid near the surface, at any instant a certain number of the "chemically adsorbed" ions are "covered" by ions of opposite charge. In the liquid near the surface there are always a number of free ions equivalent in amount to the "uncovered" chemically adsorbed ions on the surface. The total amount of ions of opposite sign both "bound" and

* Communicated by Prof. F. G. Donnan, F.R.S.

"free" is equivalent to the amount of ions "chemically adsorbed." These "free" ions form the second sheet of the double layer. It is evident that as a result of their thermal motion the mean distance between the two layers will be greater than " x ."

The charge of the surface was treated as due to discrete charged particles widely separated from each other compared with molecular dimensions. It was shown in the previous paper that this view gives a rational explanation of the fact that a reversal of the charge of a surface can be brought out only by polyvalent ions of opposite charge.

The equilibrium conditions were discussed and the equations deduced were shown to be in agreement with the valency rule, the influence of the mobility of the oppositely charged ion, and with the influence of concentration on the charge of the surface. Only the theoretically simplest case has been discussed in the earlier paper. In the present paper the more important facts connected with the adsorption of ions are discussed from this point of view, and it will be seen that this view gives a simple explanation of most of the general conclusions already arrived at on experimental grounds.

Theories of Adsorption.

Before proceeding to discuss the adsorption of ions it will be convenient to deal briefly with the different views advanced to account for adsorption in general. The withdrawal of a solute from a solution by a solid may be the result of the formation, of definite chemical compounds, of solid solutions, of mixed crystals and surface-condensation. In many cases all these changes are simultaneously present. In this paper the word "adsorption" denotes condensation or combination, at the surface only, without the interpenetration of the adsorbed substance throughout the mass of the adsorbent (Mecklenburg's criterion, *Z. Phys. Chem.* lxxxiii. p. 609 (1913) : *cp.* also the sense in which the term is used in deriving Gibbs's equation).

Faraday (*Phil. Trans.* cxiv. p. 55 (1834)) in his well-known explanation of the catalytic combination of hydrogen and oxygen on platinum surfaces, remarks "that they are dependent upon the natural condition of gaseous elasticity combined with the exertion of that attractive force, possessed by many bodies, especially those which are solid, in an eminent degree, and probably belonging to all, by which they are drawn into association more or less close, without at the same time undergoing chemical combination though often

assuming the condition of adhesion, and which occasionally leads under very favourable circumstances, as in the present instance, to the combination of bodies simultaneously subjected to this attraction." It is remarked further "that the sphere of action of particles extends beyond those other particles with which they are immediately and evidently in union, and in many cases produces effects rising into considerable importance." These remarks of Faraday mean, in modern terminology, that there is a sort of combination at the surface and that the transitional layer is more than one molecule thick. The subsequent views are in a way developments of this conception.

Gibbs treated adsorption from the standpoint of thermodynamics. A number of important investigations has been carried on by Milner (*Phil. Mag.* [6] xii. p. 96 (1907)), Lewis (*Phil. Mag.* [6] xv. p. 506 (1908)), *ibid.* xvii. p. 466 (1909)), and Donnan and Barker (*Proc. Roy. Soc. Lxxxv. A.* p. 552 (1911)). The present position is that the amount adsorbed is often considerably greater than what could be expected from Gibbs's equation.

J. J. Thomson ('Applications of Dynamics to Physics and Chemistry') showed that it follows from Laplace's theory of capillarity that in the surface layer between two liquids, chemical actions may take place which are absent in the bulk of the liquids.

Lagergren (*Bihang K. Svenska Vet. Hand.* xxiv. p. 11, No. 415 (1898)) considers that adsorption in the surface of solids in contact with aqueous solutions is due to the compressed state of the water in the surface layer.

On the experimental side the work of Freundlich and his collaborators—[*Kapillar-Chemie*, 1909; *Z. Phys. Chem.* lix. p. 284 (1907); lxvii. p. 538 (1909); lxxiii. p. 399 (1910); lxxxiii. p. 97 (1913); lxxxv. p. 398 (1913); xc. p. 681 (1915); *Koll.-Chem. Beihefte*, vi. p. 297 (1914); see also Schmidt, *Z. Phys. Chem.* lxxiv. p. 689 (1910); lxxvii. p. 641 (1911); lxxviii. p. 667 (1912); lxxxiii. p. 674 (1913); xci. p. 103 (1916). In the last-mentioned paper Schmidt and Hinteler conclude that Freundlich's equation represents their experimental data better than that of Schmidt]—and of others, have shown that adsorption-equilibria can be generally expressed in terms of the well-known equation of Freundlich:

$$x/m = \alpha \cdot c^{1/p}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Freundlich expressed the opinion that adsorption is mainly due to a decrease in surface tension as suggested by Gibbs.

In the case of adsorption of gases by solids, Arrhenius (*Medd. f. k. Vet. Nobelinstitut*, ii. N. 7 (1911); *Theories of Solution*, 1912, pp. 55-71) has drawn attention to the parallelism between the van der Waals's coefficient " a " for the different gases and the amounts of these gases adsorbed by charcoal, and he believes that this is definite evidence of the compressed state of the surface layer. At the same time he lays stress on the chemical aspect—namely, that in addition to the attractions between the molecules of the gas in the surface layer, one has to consider the chemical attraction of the surface atoms and the molecules of the gas.

Recently, Williams (*Proc. Roy. Soc.* xvi. A. p. 287 (1919); xcviii. A. p. 223 (1920); also *Trans. Far. Soc.* x. p. 155 (1914), in which complete references to the literature on negative adsorption are given) has treated adsorption from the points of view of Lagergren and of Arrhenius in a number of interesting communications.

It may be mentioned here that the disagreement of observations with calculations from Gibbs's equation is at least in part due to the fact that only one source of change in the free energy of the surface layer is taken into account. In the simplest case of the interface, liquid-saturated vapour (one component system), it is open to objection whether " γ " denotes the total change in free energy of an isothermal and reversible-formation of unit surface. Bakker (*Z. Phys. Chem.* lxxviii. p. 684 (1910)) has pointed out that if the density of the surface layer is different from that of the liquid in bulk a second term is necessary to represent the change in free energy.

It is possible that in this particular case this second term is negligible in comparison with " γ ," the tension per unit length at low temperatures, but at high temperatures " γ " has a low value and the saturation pressure is very great, so that the second term may be even more important.

Williams (*Proc. Roy. Soc. (Edinburgh)*, xxxviii. p. 23 (1917-18)) has drawn attention to the effect of the variation of the surface of an adsorbent when adsorbing—a factor which is very often neglected.

Lewis (*Z. Phys. Chem.* lxxiii. p. 129 (1910); also Partridge, 'Text-book of Thermodynamics,' p. 473 (1913)) has discussed the influence of a variation in the electric density on the surface on the form of Gibbs's equation.

These may be called the physical theories of adsorption. The difficulty in accepting them as general theories of adsorption is that they attempt to explain adsorption in terms of a single physical factor; *e. g.* diminution in surface energy

or a layer under great internal pressure. The necessity for recognizing the existence of a sort of chemical interaction (as Arrhenius has suggested) becomes evident when one considers the specific nature of adsorption processes. This point has been justly emphasized by Bancroft in recent years. Besides his papers in the 'Journal of Physical Chemistry,' compare 'Applied Colloid Chemistry,' 1921, p. 111).

The chemical point of view has been put clearly by Langmuir (J. Amer. Chem. Soc. xxxviii. p. 2221 (1916); xxxix. p. 1848 (1917)). He believes that adsorption is due to the chemical affinities of the surface atoms. Considering the thermodynamic equilibrium between molecules of a gas at the surface and those in the surrounding gas he has deduced the following equations correlating the variation of the adsorbed amount with its pressure,

$$\theta_1 = \frac{\alpha \cdot \mu}{\nu_1 + \alpha \cdot \mu};$$

where " θ_1 " is the fraction of the solid surface covered and is a measure of the amount adsorbed, ν_1 is the rate at which the gas would evaporate if unit area of the surface were completely covered, " μ " is the number of gas molecules striking unit area of the surface per second and is given by

$\mu = 43.75 \times 10^{-6} \frac{P}{\sqrt{M \cdot T}}$, and " P " denotes the pressure of

the gas, " T " its absolute temperature, and " M " its molecular weight. α denotes the fraction of the total number of collisions of the molecules of the gas that leads to a condensation on the surface; it is usually close to unity and evidently can never exceed unity. Some interesting applications of his theory to catalysis of gaseous reactions by solid surfaces are given. This theory explains many phenomena which are otherwise difficult to understand.

Michaelis and Rona (*Bio-Chem. Zeitsch.* xcvii. pp. 56, 85 (1919)) conclude from the investigations of Michaelis and his co-workers that the assumption of special forces at the surface fails to account for the facts and that adsorption is the result of chemical affinity.

I. The Adsorption of a Constituent Ion by a Precipitate.

The adsorption of ions is different from the adsorption of neutral molecules or groups in that it introduces a new factor—an electrically charged surface. The variation in the electric charge enables us to follow the net effect of the adsorption of the two ions, as the electric charge depends

only on the total number of ions (of both signs) fixed per unit area of the surface. Kataphoretic and electro-endosmotic experiments give us a quantitative idea of the relative adsorption of both ions.

The electric charge helps to peptize the adsorbent, and a qualitative idea of the adsorption of ions can be formed from peptization by electrolytes. An insoluble precipitate formed by the union of two oppositely charged ions has a marked tendency to adsorb its component ions. In many cases the connexion between the adsorbed ion and the electrical charge has been established. These instances have been given in the earlier paper. The nature of the chemical forces responsible for this adsorption has also been defined. Instances of adsorption of ions as judged from peptization by electrolytes are given below.

Bancroft (Rep. Brit. Assoc. p. 2 (1918)) remarks :—" It seems to be a general rule that insoluble electrolytes adsorb their own ions markedly, consequently a soluble salt having one ion in common with a sparingly soluble electrolyte will tend to peptize the latter. Freshly precipitated silver halides are peptized by dilute silver nitrate or the corresponding potassium halide, the silver and the halide ions being adsorbed strongly. Many oxides are peptized by their chlorides and nitrates, forming so-called basic salts. Sulphides are peptized by hydrogen sulphide. . . . The peptization of hydrous oxides by caustic alkali can be considered as a case of adsorption of a common ion or as the preferential adsorption of hydroxylion. Hydrous chromic oxide gives an apparently clear green solution when treated with an excess of caustic potash ; but the green oxide can be filtered out completely by means of a collodion filter, a colourless solution passing through."

" Hantzsch considers that hydrous beryllium oxide is peptized by caustic alkali, copper oxide is peptized by concentrated alkali, and so is cobalt oxide. In ammoniacal copper solutions part of the copper oxide is apparently colloidal and part is dissolved. Freshly precipitated zinc oxide is peptized by alkali, but the solution is very unstable" (*cp.* also negative hydroxide sols—Freundlich and Leonhardt, *Koll. Chem. Beihefte*, vii. p. 172 (1915)).

At least in some of these cases the formation of new complex anions is possible, and it is not definitely known to what ion the peptization is due. Regarding the peptization of stannic acid gel by small quantities of alkali, Zsigmondy (*Kolloidchemie*, p. 122 et seq. (1920) : also Varga, *Koll. Chem. Beihefte*, xi. p. 26 (1919)) remarks : " Dieses kann

sowohl auf Adsorption des gebildeten Kaliumstannats wie auch darauf zurückführen sein, das Kaliumhydrat mit den Oberflächenmolekülen der Zinnsäureprimärteilchen in Reaktion tritt, wobei diese von der Oberfläche der Primärteilchen festgehalten werden."

The view suggested by the writer to account for the adsorption of a common ion, leads one to expect that ions which can displace one of the constituent ions in the crystal lattice should also be adsorbed. Marc (*Z. Phys. Chem.* lxxx. p. 641 (1913)) has observed that crystalline adsorbents adsorb crystalloids to any marked degree only when they can form mixed crystals with them and are isomorphous with them. Paneth and Horowitz (*Physik. Zeitsch.* xv. p. 924 (1914)) have noticed that of the radio elements those only will be adsorbed that can form insoluble salts with the common ion of the adsorbent and can also form mixed crystals with the adsorbent. This kind of adsorption is somewhat different from the type we have considered for, as Paneth has pointed out in his case, an actual interpenetration of the two non-common ions is occurring in the crystal lattice. Thus radium is taken up by barium sulphate giving out to the solution barium ions in exchange. Such an interchange will not impart a charge to the surface.

Attention may also be drawn to the explanation advanced by Bradford (*Biochem. J.* x. p. 169 (1916); xi. p. 14 (1917)) to account for zonal precipitations, first studied by Liesegang. Bradford thinks that the adsorption of a constituent ion is responsible for their formation. From the numerous instances given above, this conception seems to be quite plausible. It is probable that other factors have also an influence on the process (Hatschek, *Brit. Assoc. Rep.* p. 24 (1918)).

II. *The Variation of the Density of the Electric Charge with the Concentration of an Electrolyte.*

In the previous paper the particular case when the charge of the surface is due to strong chemical adsorption of ions of one kind and when the added electrolytes have not any ions, subject to the chemical affinity of the surface atoms, has been fully treated. In this case it was assumed that the number of ions adsorbed at the surface by chemical affinity remains constant. The experimental data of Elissafoff on glass and quartz agree well with equations deduced from these assumptions, on the basis of the theory of electrical adsorption.

The general case, however, is that :

(a) At low concentrations the density of the charge on the surface at first increases to a maximum and at higher concentrations falls gradually towards a null value when the oppositely charged ions are monovalent.

(b) On the other hand, when the oppositely charged ions are multivalent or complex organic ions the charge passes through a null value, becomes reversed in sign, and again reaches a second maximum, after which it falls slowly (Ellis, *Z. Phys. Chem.* lxxviii. p. 321 (1911); lxxx. p. 597 (1912); lxxxix. p. 145 (1914); Powis, *Z. Phys. Chem.* lxxxix., pp. 91, 179 (1914); Riety, *Compt. Rend.* cliv. pp. 1411, 1215 (1912); clvi. p. 1368 (1913); Young and Neal, *J. Phys. Chem.* xxi. p. 1 (1917); Krøyt, *Versl. Kon. Akad. v. Wetensch. Amsterdam*, 27th Jun. 1914, also *Koll.-Zeitsch.* xxii. p. 81 (1918)).

The usual explanation is as follows:—

The adsorption-isotherms for the two ions can be written as

$$\frac{x_K}{m} = \alpha_K \cdot c^{\beta_K}, \text{ and } \frac{x_A}{m} = \alpha_A \cdot c^{\beta_A}, \quad . \quad . \quad . \quad (3)$$

where the subscripts A and K refer to the anion and the cation respectively. To explain the increase in the charge at low concentrations it has to be assumed that

$$\alpha_A > \alpha_K \quad \text{and} \quad \beta_A < \beta_K. \quad . \quad . \quad . \quad (4)$$

Thus in a paper read at the Discussion on Colloids arranged by the Faraday and the Physical Societies of London, Svedberg remarks: "Now as a rule, it happens that for the two ions of a salt both α and β have different values, e. g.

$$\alpha (\text{cation}) < \alpha (\text{anion})$$

$$\beta (\text{cation}) > \beta (\text{anion})."$$

It is clear that the equation of the adsorption-isotherm can be reconciled with the first increase in the charge. But two objections can be raised against this empirical point of view. In the first place, no reason is given why the constants α and β shall have generally the relative values assumed above for the cation and the anion. Secondly, these assumptions cannot explain the second maximum charge and the subsequent decrease observed with multivalent ions of opposite charge. It will now be necessary to assume that

$$\alpha_A < \alpha_K \quad \text{and} \quad \beta_A > \beta_K, \quad . \quad . \quad . \quad (5)$$

in direct contradiction to the assumptions already made

(*cp.* (4)). Besides, one cannot get any idea as to why the anion is generally more strongly adsorbed at low concentrations.

The facts can, however, be explained as follows:—

The negative charge of surfaces in contact with water is to be sought for in the chemical natures of the anions and the cations. The simpler electrolytes (excluding dyes and complex organic ions) have cations whose chemical behaviour can be referred simply to the tendency of the component atom (*e.g.* of the alkali and alkaline earth metals) to pass into the ionic state. These ions do not form any complex ions. They form only one type of compounds that are stable in aqueous solutions, namely, electrolytes with the atom existing as a positively charged ion through the loss of one or more electrons. On the other hand, the anions in general form types of compounds other than electrolytes, and also form complex ions. It is, therefore, possible to imagine that anions are subject to the chemical affinity of the surface atoms and that the chemical action on the cations is relatively small. Complex cations like those of the basic dyes should, for the same reason, be easily adsorbable. This is a well-known fact.

If now, the assumption is made that the chemical affinity acting on the anion of the electrolyte added is stronger than the electrostatic attraction of the surface on the cation, the observed variation of the charge with the concentration of the electrolyte is easily accounted for. This case corresponds to a strongly marked maximum of a negative charge at a low concentration of the electrolyte.

The initial charge of a surface in contact with pure water can be due either:

- (a) to the strong adsorption of an ion of a minute quantity of suitable electrolyte associated with the solid,
- (b) or to the adsorption of hydroxyl ions from water.

On the addition of an electrolyte the density of the electric charge will increase at low concentrations because of the chemical adsorption of the anion. The electrical adsorption of the cation is smaller as the chemical adsorption has been assumed to be stronger. Besides, the electric charge of the surface is also not at its maximum. As the surface becomes more and more covered by the anions the rate of adsorption dx/dc —where “ dx ” is the increase in the amount adsorbed per unit surface due to an increase in the concentration “ dc ”—rapidly decreases. Also, the electric charge repels the anions, and those only can strike on it that have sufficient

kinetic energy to overcome the potential of the double layer. The number of collisions is thus not proportional to the concentration but rises more slowly. Near about the point where the surface becomes saturated the value of dx/dc will be almost zero (*cp.* the shape of the adsorption-isotherms of Freundlich, Arrhenius, and Langmuir). On the other hand, the electrical adsorption increases continually with the concentration and the increase of the charge. It is apparent that soon a balance will be reached between the chemical adsorption of the anion and the electrical adsorption of the cation. The minimum charge will correspond to the stage when dx/dc for the cation is just equal to dx/dc for the anion.

Beyond this concentration the charge will decrease rapidly, and when the surface has been saturated with the anion the subsequent variation in the charge is simply due to electrical adsorption. The reversal of the charge by electrical adsorption has been discussed in the earlier paper. It is necessary to add that as the electrically adsorbed *polyvalent* cations impart a positive charge to the surface, the adsorption of the cation decreases and the *electrical adsorption* of the anion becomes possible. As long as there is a positively charged surface the adsorption of the anion will increase more rapidly with the concentration than that of the cation. *A second maximum will thus be reached and a decrease in the charge will follow.* The electrical adsorption of the anion is small because of the smallness of the positive charge and an initially existing negatively charged surface. A further reversal of the charge is not possible, and, in fact, has never been observed.

III. *The Action of Acids and Alkalies.*

The works of Perrin and of others (*J. Chim. Phys.* ii. p. 601 (1904); iii. p. 50 (1905); Haber and Klemensiewicz, *Z. Phys. Chem.* lxxvii. p. 385 (1909); Cameron and Oettinger, *Phil. Mag.* [vi.] xviii. p. 586 (1909)) have shown that hydrogen and hydroxyl ions behave exceptionally in that they impart to the surface a charge of the same sign as they carry. This behaviour is in contrast to that of the other univalent ions.

Perrin attributes their singular activity to the smallness of their radii. In order to explain the presence of these ions, in excess, in the surface layer, it is necessary to assume some sort of a restraining force acting on them at the surface.

Haber and Klemensiewicz consider that there is an adsorbed layer of water in the surface by virtue of which the

solid acts as a sort of combined hydrogen and oxygen electrode. They treat the subject from the points of view of thermodynamics and Nernst's theory of electrolytic solution tension. It has been pointed out by Freundlich (and Elissafoff, *Z. Phys. Chem.* lxxix. p. 407 (1912)) that hydrogen and hydroxyl ions are not the only ions which impart a charge to the surface. In many cases, acids have been observed not to reverse the charge at all. Many substances have a negative charge in contact with pure water. These facts show that selective adsorption of hydroxyl ions has also to be considered.

This thermodynamic treatment from the point of view of Nernst's theory does not attempt to explain electro-endosmosis. For this purpose it is necessary to conceive of an electrical double layer, of which the layer imparting a charge to the surface is fixed relative to the mobile second layer.

Freundlich, and Freundlich and Rona (*Koll. Zeit.* xxviii. 5, p. 240 (1921); *Kgl. Preuss. Akad. Wiss. Berlin*, 1920, p. 397, C. 1920, iii. p. 26) have shown that the potential measurements by Haber's method are not in agreement with those measured by electro-endosmotic experiments. They therefore suggest that there are two distinct drops in potential as one passes from the solid to the liquid (glass to water). The first drop is wholly in the solid and is probably of the nature associated with the Nernst theory of electrolytic solution-tensions.

The second drop is in the liquid and composes the Helmholtzian double layer which it is necessary to assume to explain electro-osmosis and cataphoresis.

At the same time the characteristic effects of hydrogen and hydroxyl ions on neutral substances like barium sulphate, silver chloride, naphthalene, etc., point strongly to the correctness of Haber's fundamental assumption that the explanation is to be sought in the equilibrium between the hydrogen and hydroxyl ions in the adsorbed layer of water and those in the bulk of the liquid.

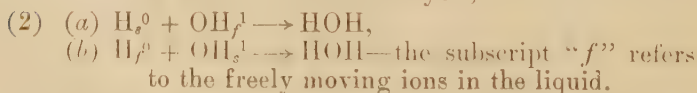
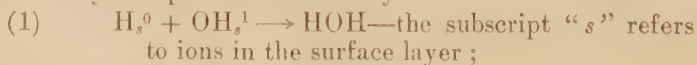
Williams (*Proc. Roy. Soc.* xcvi. A. p. 223 (1920)) has recently suggested that the layer of water adsorbed on a charcoal surface is under great internal pressure (about 10,000 atmospheres). Applying Planck's equation he shows that the effect of this pressure will be to increase the concentration of hydrogen and hydroxyl ions in this layer. This increased concentration will set up a diffusion potential. He draws attention to the difficulties in accepting this view of the origin of the potential difference at the surface. In the instances considered by Haber and Perrin, the solid has

little or no potential difference in contact with pure water, and the considerations developed by Williams are not applicable.

CASE 1.—*The surface is inert.*

We shall assume that the atoms in the surface do not exert any chemical affinity on hydrogen and hydroxyl ions as such, or on the dissolved acid (or alkali) with which it may be in contact. The adsorbed water molecules behave as a solid layer, being held by strong chemical forces (Haber, *loc. cit.*; Hardy, Proc. Roy. Soc. lxxxiv. B. p. 217 (1911)). It is clear that the surface will be neutral in contact with pure water. The molecules of water in the adsorbed layer are in thermodynamic equilibrium with those in the bulk of the liquid. It is reasonable to imagine that a transfer of an electron is taking place between the hydrogen atom and the hydroxyl group in the water molecules in the surface layer, as it does in the molecules in the liquid. That is, the water molecules are dissociating into ions at a definite rate. Let " nx " be the number of water molecules (in the adsorbed layer) passing into the ionized phase per unit area per second. For equilibrium, as many hydrogen and hydroxyl ions are uniting to form neutral water molecules. Since the adsorbed water molecules behave as a solid layer, recombinations would take place mostly between adjacent hydrogen and hydroxyl ions. The recombination will be extremely rapid. It can be assumed that at any instant the number of hydrogen or hydroxyl ions actually remaining free in the surface will be a negligible fraction of the total number of water molecules.

The neutralization of the ions being formed in the surface layer can also be brought about by impinging hydrogen or hydroxyl ions present in the liquid. In contact with pure water the probability of such collisions is small, for the concentration of hydrogen and hydroxyl ions is extremely small. Thus neutralization of the ions being formed in the surface layer is possible in two ways :



In contact with pure water, neutralizations according to scheme 2 are small in number. Also 2 (a) and 2 (b) are equally probable. Consequently the numbers of H_s^0 and OH_s^1 remaining in the surface at any instant will be equal, and the surface will be neutral.

When an acid is added to the water the neutralizations according to scheme 2 (a) will be completely negligible, but those according to scheme 2 (b) will not be so. The total number of neutral molecules of water formed in the surface is still equal to " x ," but a number of them is now being formed according to 2 (b). Corresponding to the number of neutralizations according to 2 (b), a number of hydrogen ions will remain in the surface layer in excess of the number of hydroxyl ions. The rate at which 2 (b) proceeds thus determines the free charge on the surface. An equivalent number of anions remain unneutralized in the liquid and form the second mobile sheet of the double layer.

The free charge on the surface will evidently increase with rise in the concentration of hydrogen ions in the solution. There are, however, two factors opposing this increase in the charge of the surface.

A. The proportion of hydrogen ions striking on the surface diminishes as the positive charge of the surface increases. Only those ions which have sufficient kinetic energy to overcome the electrical repulsion can reach it. If ϵ be the potential of the double layer in C.G.S. units, then the number of collisions of the ions per unit surface per second is proportional to

$$U_{H^+} \cdot C_{H^+} \cdot e^{-\epsilon \cdot E / KT}, \quad (6)$$

where C_{H^+} denotes the concentration of free hydrogen ions in the liquid, " E " is the electronic charge in C.G.S. units, T is the absolute temperature, U_{H^+} is the mobility of the hydrogen ions in water, and $K = R/No$, where " R " is the gas constant and No the Avogadro number.

B. The other factor that tends to diminish the charge of the surface is the electrical adsorption of the anion of the acid added to the solution. That this plays an important part will be evident from the following examples taken from the observations of Perrin :—

Substance.	Electrolyte.	Rate of Electro- endosmotic outflow.
Al ₂ O ₃	M/1000 HCl	+ 110
"	M/1000 citric acid	+ 5
"	M/1000 HNO ₃ (or HCl)	+ 100
"	M/1000 H ₂ SO ₄	+ 15
CrCl ₃	M/1000 HNO ₃	+ 85
"	M/1000 H ₂ SO ₄	+ 21
"	M/500 HCl	+ 90
"	M/1000 H ₂ C ₂ O ₄	+ 30
"	Feebly acid with HCl	+ 75
"	Solution of KH ₂ (PO ₄) with approximately the same number of free hydrogen ions as above	+ 7

Both these factors tend to diminish the rate of increase of the charge with rise in the concentration of hydrogen ions. For acids with simple univalent anions, the electrical adsorption at low concentrations can be left out of account in view of the excessive mobility of the hydrogen ions.

A quantitative relationship can now be obtained between the charge on the surface and the concentration of the acid. Let x^1 be the rate of neutralization according to 2 (b) above. We have then

$$x^1 = K \cdot x \cdot C_{H^0} \cdot e^{-\epsilon \cdot E/kT}, \quad (7)$$

where k is a constant.

The density of the charge on the surface is proportional to x^1 —which is a measure of the number of hydrogen ions remaining in excess in the surface. If the thickness of the double layer remains constant then the potential of the double layer is proportional to the density of the charge: that is, to x^1 .

When all the hydroxyl ions in the surface layer are being neutralized according to 2 (b) the surface will have a maximum charge determined by “ x .”

Putting $x^1/x = \theta$, since “ x ” is a constant, we have

$$\epsilon \propto \theta, \quad (8)$$

and θ represents the ratio of the hydrogen ions present in excess at any instant in the surface layer to the maximum number possible when the neutralization takes place only according to 2 (b). The potential of the double layer can be written as

$$\epsilon = k_1 \cdot x^1 = k_2 \cdot \theta = k_3 \cdot C_{H^0} \cdot e^{-\beta \cdot \theta/T} \cdot U_{H^0}, \quad . . . (9)$$

$$\text{or} \quad \theta = k_0 \cdot C_{H^0} \cdot e^{-\beta \cdot \theta/T} \cdot U_{H^0}, \quad (10)$$

where k_1 , k_2 , k_3 , k_0 and β denote constants.

Similarly, for alkali solutions we have

$$\theta = k_0 \cdot C_{OH^1} \cdot e^{-\beta \cdot \theta/T} \cdot U_{OH^1}, \quad (11)$$

The maximum charge, being determined by x , will be the same with alkali as with acid. Of course, the influence of the oppositely charged ion in the acid or the base is being neglected.

CASE 2.—*The surface is not chemically inert: preferential adsorption of one ion is possible.*

A review of the literature shows that surfaces in contact with water are seldom neutral. They are generally more or less negatively charged. This is intelligible in view of the

chemical reactivity of the hydroxyl group. The presence of the potentially tetravalent oxygen atom possibly leads to a selective adsorption of hydroxyl ions by most surfaces. Thus glass and quartz have a marked negative charge in contact with water (*cp.* Elissaffoff). On the addition of an acid the electrostatic forces will produce a diminution of the charge. The electrical adsorption of hydrogen ions by hydroxyl ions cannot be distinguished from the recombination of hydrogen and hydroxyl ions to form neutral molecules of water. This is confirmed by the fact that the equation of electrical adsorption (*cp.* previous paper) satisfactorily represents the diminution of the charge.

Perrin (*loc. cit.*) found that, excepting alumina and chromium chloride, all other substances (naphthalene, silver chloride, boric acid, sulphur, salol, carborundum, gelatine, and cellulose) show a preferential adsorption of hydroxyl ions. The surfaces have a negative charge even in contact with acid solutions. He also found that at higher concentrations of the acid the surface acquired a positive charge. Elissaffoff, McTaggart, Ellis, Powis, and others could not observe this reversal in their investigations. Electrical adsorption of hydrogen ions cannot lead to a reversal of the charge. The reversal (or the non-reversal) of the charge becomes intelligible if it is assumed that the considerations set forth in deducing equations (8) or (9) are correct.

In contact with pure water the surface has a layer of adsorbed water and a number of hydroxyl ions. The amount of hydroxyl ions adsorbed by the surface will, in general, be small, as the concentration of the hydroxyl ions is very small in pure water. If, however, the adsorption is very strong the surface will have a considerable negative charge. On the addition of an alkali the negative charge of the surface will increase, due to two reasons:

(1) the preferential adsorption of hydroxyl ions will increase, and

(2) the number of hydrogen ions being formed at the surface will be more and more neutralized by hydroxyl ions in the liquid (*cp.* scheme 2(a)). A maximum will be reached when the surface is saturated by preferential adsorption and when $\theta=1$ in equation (9). The maximum charge per unit area can be written as

$$E_m = x + y \text{ (for alkali), } \dots \dots (12)$$

where "x" corresponds to the charge when $\theta=1$ in equation (8) and "y" is proportional to the number of

hydroxyl ions the surface can adsorb per unit area when it is saturated.

Since the chemical adsorption of hydrogen ions is assumed to be absent, on the addition of an acid the negative charge will decrease owing to electrical adsorption till the surface becomes neutral. At this concentration of the acid, the surface has an adsorbed layer of water, and an equal number of hydrogen and hydroxyl ions. An increase in the positive charge cannot be due to electrical adsorption of the univalent hydrogen ions (*cp.* previous paper). The increase in the charge is due to the neutralization of the hydroxyl ions being formed in the surface by impinging hydrogen ions, as represented in scheme 2 (b) above.

The maximum charge E_m for an acid will, therefore, be equal to "*x*." *The maximum charge due to acids thus gives a measure of the hydration of the surface.* The difference between the maximum charge observed with acid and with alkali gives a measure of the amount of hydroxyl ions that is required to saturate the surface.

In the preceding discussion, the chemical and electrical adsorption of the anion of the acid has been left out of account for the sake of simplicity. If the initial negative charge of the surface in contact with pure water is considerable the electrical adsorption can be complete only at high concentrations of the acid, *i. e.*, the surface will be neutral at a high concentration of the acid. The electrical adsorption of the anion is no longer negligible. A reversal of the charge, though theoretically possible, may not be actually observed owing to the great concentration of the anion.

The reversal is thus dependent on:—

- (1) a large value of *x*, and
- (2) a small value of *y*.

A non-reversal is to be expected when the opposite is the case, *i. e.*,

- (1) a small value of "*x*," and
- (2) a large value of "*y*."

A regular transition from marked reversal to non-reversal can be observed in Perrin's work. With cellulose he also does not record a reversal of the charge. It is to be expected from the preceding considerations that non-reversal will not be observed when the concentration of the acid required to render the surface neutral is comparatively high, *i. e.*, the anion concentration is high. The concentration of the acid in the case of cellulose is the greatest recorded by Perrin.

The chemical adsorption of the anion is also not to be neglected. The experimental data on this subject are meagre. The various points raised here can be experimentally elucidated. As shown above, the standpoint developed in this paper can correlate all the observed facts. Besides, it gives a definite idea of the electrical double layer.

Adsorption of electrolytes.

In the preceding sections the adsorption of ions has been considered with reference to the electrical charge of surfaces in contact with aqueous solutions of a single electrolyte. The electric effects accompanying the adsorption of ions have enabled us to follow the total adsorption of ions of both signs. In considering the adsorption of ions measured by chemical means it is important to remember the influence of the adsorption of the solvent pointed out by Arrhenius, Bancroft, Williams, and others.

The amount adsorbed is small and the analytical measurement is difficult. For this reason, investigations have centred round adsorbents with great adsorbing power and substances which are strongly adsorbed. Often it happens, that if a substance is used in a satisfactorily pure state it does not have the necessary specific surface to make the estimation of the adsorbed amount possible. As a result adsorbents generally contain small amounts of other substances. The importance of these impurities has been pointed out by some investigators.

Michaelis and Freundlich and their co-workers have done systematic work in this field. Their investigations have brought out the following regularities:—

(a) The electric charge of the solid influences the adsorption. Thus Michaelis and Lachs (*Z. Elektro-Chem.* xvii. pp. 1, 917 (1911)); *Biochem. Zeitsch.* xxv. p. 359 (1910)), and Davidsohn, *Biochem. Zeitsch.* liv. p. 323 (1913)) found that in contact with acid solutions charcoal adsorbs anions strongly and does not adsorb cations. The reverse happens in the case of cations. Freundlich and Poser (*Koll. Chem. Beihefte*, vi. p. 297 (1914)) undertook an extensive investigation, and they agree with Michaelis as to the electro-chemical nature of the adsorption.

(b) The chemical nature of the adsorbent has a specific action.

Michaelis and Rona (*Biochem. Zeitsch.* xcvii. pp. 57, 85 (1919)) believe that adsorption is due to chemical affinity. They mention that charcoal has a great capacity for adsorbing substances containing a chain of carbon atoms. (Cp. Abderhalden and Fodor, *Fermentforschung*, ii. p. 74 (1917).)

Freundlich and Poser (*loc. cit.*) found that the nature of the adsorbent plays an important part in determining the adsorbability of a dye.

Both Michaelis and Freundlich agree that at least two types of adsorption of ions can be recognized.

(c). Exchange or displacement of ions already adsorbed by ions of a second electrolyte (*cp.* Freundlich, "Verdrängende Ionenadsorption" and Michaelis, "Austausch-Adsorption"). Michaelis (*Z. Electrochem.* xiv. p. 353 (1918)) considers that a substance like mastic, or kaolin (holus), acts as a "zweier electrode" (a binary electrode). Thus kaolin has a slow-moving anion (silicate ion) anchored on its surface and tends to send hydrogen ions into the solution under a definite electrolytic solution tension. Freundlich points out (and Poser, *loc. cit.*) that other cations can displace the hydrogen ions and form undissociated complexes (and Elissaffoff, *Z. Phys. Chem.* lxxix. p. 385 1912).

(d) An adsorbent which contains some adsorbed electrolytes need not be necessarily saturated. In this case, besides an exchange of ions, primary adsorption of ions is possible. This also applies to substances which act as binary electrodes in the sense in which the word has been used by Michaelis. He considers that, besides adsorption through exchange of ions, there is only one other type of adsorption, namely, adsorption of both ions in equivalent amounts ("Äquivalent Adsorption").

One other fact has been emphasized by these authors.

(e) It is the irreversible nature of electro-chemical adsorption. The well known instance of the adsorption of hydrogen sulphide by metal sulphides studied by Linder and Pieton (*T.* lxvii. p. 163 (1895) ; Whitney and Ober, *J. Amer. Chem. Soc.* xxiii. p. 842 (1901)) can be mentioned. The adsorbed substance does not come out in solution when the adsorbent is brought in contact with pure water.

(f) Lastly, there is no clearly established instance in which hydrolytic splitting up of neutral salts such as potassium chloride has been observed through adsorption.

Theories regarding the Exchange of Ions.

The conception of an adsorbent acting as a binary electrode, suggested by Michaelis, is not of much help in explaining the exchange of ions and other peculiarities of the adsorption of electrolytes. The relationship between the adsorption of ions, electro-endosmotic cataphoresis, and precipitation of colloids has been established beyond doubt. The only theory

that attempts to correlate them is that due to Freundlich. This view is an extension of Michaelis's idea referred to above. The adsorbent (or colloidal particle) is regarded as a great multivalent ion (*cp.* Billiter, *Z. Phys. Chem.* xlv. p. 307 (1903 ; Duclaux, *J. Chim. Phys.* v. p. 29 (1907)). The following extract shows clearly their standpoint (Freundlich and Elissaffoff, *loc. cit.* p. 411):—

„Die Ladung soll nun durch die verschieden grosse Lösungstension der Ionen des schwerlöslichen festen Stoffs zustande kommen, aus dem das suspendierte Teilchen, bzw. die Wand besteht. Nimmt man als Beispiel das Glas, so hat man an der Oberfläche desselben eine Schicht von gelöstem, oder bzw. in wasser gequollenem Silikat: die K- und Na-Ionen haben eine grosse Lösungstension und bilden eine äussere Schicht, die schwerlöslichen, langsam diffundierenden (vielleicht auch stark absorbierbaren) Silikationen bilden eine innere Schicht, die mit dem festen Stoff verbunden wie ein vielwertiges Ion sich verhält. Der wesentliche Unterschied gegen ein gewöhnliches Ion liegt darin, dass wegen der Grösse Grenzflächenwirkungen eintreten, die Konzentration ist in der Umgebung nicht so homogen, sondern es sind durch Adsorption hervorgerufene Konzentrationsunterschiede vorhanden.

„Für zwei Ionen gilt nach der Massenwirkungsgesetz (Anion). (Kation) = k (nichtdissociertes Salz), deshalb auch für das mikronische, vielwertige Anion des als Beispiel betrachteten Glases.

„(Vielwertiges Anion). (Kation) = K (nichtdissociierter Stoff). Es wird also von der Konzentration der Kationen die Konzentration des vielwertigen Anions, d.h. auch die Zahl der auf der Grenzfläche vorhandenen Ladungen abhängen.

„Die Kationenkonzentration, um die es sich hier handelt, wird aber in erster Linie die der nächsten Umgebung der Grenzfläche, d.h. die Adsorptionsschicht sein. Die adsorbierte Menge Kation wird also für die Konzentration des vielwertigen Anions, d.h. für die Ladung der Grenzfläche massgebend sein. Dies ist eine andere Verknüpfung von Adsorption und Potentialdifferenz an der Grenzfläche. Genau das Gleiche gilt natürlich für ein vielwertiges Kation und die adsorbierten Anionen.”

There are several difficulties in accepting this theory. Salts of alkali metals can neutralize charged surfaces at moderate concentrations ($N/10$ or $N/20$). One has to conclude that the alkali salts of these “multivalent anions” have a low solubility product. The effect of the valency of the

oppositely charged ion cannot be accounted for. The activity of the cations is generally in the following order :—



The postulates that alkali metal salts become undissociated at low concentration of the cation and that their solubility products are of the above order for a large number of diverse chemical substances, are contrary to experience. Regarded from the chemical point of view the generality of these observations cannot be explained. Besides, the conception of the suppression of the dissociation of a salt cannot explain the reversal of the charge which is met with when the oppositely charged ion is polyvalent.

The view of electrical adsorption put forth by the writer gives a definite correlated account of these various facts.

The Role of Electrostatic Forces in the Absorption of Ions.

(a) Adsorbent in contact with a single electrolyte :—

Let us consider an adsorbent, P, in contact with an electrolyte $A^+ B^-$. It is assumed that the substance P only adsorbs the anion B^- by chemical affinity. For simplicity it is also assumed that "P" is a pure chemical substance of definite composition. The amount of B^- adsorbed per unit area will depend on the concentration of $A^+ B^-$ and on the strength of the chemical affinities acting on B^- . Corresponding to the number of anions adsorbed an equivalent number of cations A^+ remain in the solution. These are held near the surface by electrostatic forces, and form the second mobile sheet of the double layer (*cp.* the earlier paper referred to). If the concentration of the electrolyte is sufficient, some of them will be fixed on the surface by electrostatic forces. These ions of opposite charge fixed on the surface by electrostatic forces will be spoken of as electrically adsorbed in the sequel. The chemical adsorption of an ion thus concentrates both ions at the surface in equal amounts. That is, the primary adsorption is an equivalent adsorption of both ions. Analytical methods cannot differentiate between the two adsorptions, but electro-osmotic and cataphoretic experiments can (*cp.* (d) above).

If the adsorption of the anion is due to strong chemical forces, perceptible amounts of the electrolyte $A^+ B^-$ will be adsorbed at very low concentrations. Even saturation may be reached at low concentrations. In such cases, if the

adsorbent with adsorbed electrolyte is suspended in pure water the adsorbed electrolyte will not be set free (*e*).

Since the primary adsorption of the ions is due to chemical affinity, the influences of the nature of the adsorbent and of the electrolyte (*b*) are intelligible.

(*b*) The addition of a second electrolyte :—

The general case when both electrolytes, $A^+ B^-$ and $C^+ D^-$, are present in all possible concentrations will be too complex. It will be assumed for the sake of simplicity that—

(1) the substance *P* adsorbs chemically the anion B^- strongly, and that the concentration of the electrolyte $A^+ B^-$ in the liquid is negligible. We are thus dealing with an adsorbent with an amount of adsorbed electrolyte in contact with a second electrolyte solution ;

(2) the atoms on the surface of the adsorbent *P* do not exert any chemical affinity on the ions C^+ and D^- .

This particular case corresponds with most actual systems, and the electrolyte $A^+ B^-$ plays the part of the “Aktiver Electrolyt” of Michaelis.

Let us now consider the effects of the electrostatic forces on the ions C^+ and D^- . A cation C^+ , when it diffuses into the double layer owing to thermal energy, will be attracted to the surface. Considering the kinetic equilibrium between the ions in the second sheet of the double layer (A^+ and C^+) and those in the liquid, it is evident that the relative proportion of A^+ and C^+ ions in the double layer will depend on (i.) their respective concentrations in the bulk of the liquid, and (ii.) their valency. The same consideration applies to the electrically-adsorbed ions A^- or C^- . At sufficiently large concentrations the whole of the mobile second layer and electrically-adsorbed ions will be formed by the ions C^+ . There will thus be an exchange of ions, and the amount of exchange will depend on the concentration of the second electrolyte. When the displacement is complete the amounts exchanged will be equivalent to the amount of B^- ions primarily adsorbed and independent of the nature of the replacing ion C^+ —a fact often observed (*cp.* Linder and Picton, *loc. cit.*; Whitney and Ober, *loc. cit.* etc.).

The ions C^+ will be positively adsorbed.

The relationship between the charge of the surface and the positive adsorption of the oppositely-charged ion is also obvious. The amount of C^+ ions absorbed depends on the

amount of the negative ions chemically adsorbed. Anything that increases the total amount of adsorbed negative ions will increase the positive adsorption of C^+ .

The reverse case, when the positively-charged ions A^+ are adsorbed chemically instead of the ions B^- , and no other ions are chemically acted on by the surface, is obvious. Negative ions will now be positively adsorbed and exchanged. This state of affairs corresponds with the statements made in (a) and (c) above.

Taking the same case again, we shall consider the effect of the electrostatic forces on the ion D^- . An ion D^- , diffusing into the double layer, will be driven out of it. So long as the potential of the double layer is sufficiently strong, a volume of the liquid equal to " Sl ," where " S " is the extent of the surface and " l " is the thickness of the double layer—will be free from the ion D^- . In other words, the concentration of D^- increases in the bulk of the liquid and a negative adsorption will take place. This will increase with the concentration of the electrolyte so long as the potential of the double layer is sufficiently strong. Since with increase in concentration the potential falls, the negative adsorption will reach a maximum. At concentrations when the surface becomes electrically neutral, there should be no negative adsorption due to electric forces. It is difficult to determine negative adsorption at high concentrations as the osmotic pressure opposes it. Also, the variations in concentration due to negative adsorption become relatively small. The experimental difficulties lie in the analytical estimation of small amounts. Only ions which can be estimated in extremely small amounts are suitable for experiment.

Estrup (*Koll. Zeitsch.* xi, p. 8 (1911)) has actually observed a negative adsorption of the oppositely-charged ion. He estimated the adsorption of the iodate, dichromate, and chromate of ammonium. Michaelis and Lachs (*Koll. Zeitsch.* ix, p. 275 (1911)) did not observe a negative adsorption with potassium chloride.

Exactly similar observations have recently been made by Bethe (*Wiener Medic. Wochsch.* 1916, Nr. 14; *Koll. Zeitsch.* xxi, p. 47 (1917)). He worked with gelatine gel, gelatine sol, and a number of animal cells. The adsorption of a basic dye is greater in weak alkaline solutions than in neutral solutions. The same is the case for an acidic dye in weak acid solutions. In alkaline solutions the adsorption of acid dyes is negative, and the same is the case with basic dyes in acid solutions. Examples of the *role* of the electrical

force in the adsorption of ions can be multiplied (*cp.* Baur, *Z. Phys. Chem.* xcii. p. 81 (1916); Michaelis and Davidsohn, *loc. cit.*).

Exchange of Bases in Soil and Soil-Acidity

It is now easy to understand the nature of the exchange of bases in soil-analysis and the cause of soil-acidity. A complete reference to the older literature is given in the following papers:—

(1) McCall, Hildebrandt, and Johnson, *J. Phys. Chem.* 1916, xx. p. 51.

(2) Rice, *ibid.* p. 214; (3) Truog, *ibid.* p. 457.

Russell (*Brit. Assoc. Rep.* 1918, p. 70) has given an excellent summary of the present position of the subject. The facts are that—

(a) Neutral solutions of salts like potassium chloride, if treated with samples of soil, give acid extracts though the extract with pure water is neutral.

(b) In a large number of cases it has been shown that there is a definite exchange of the cations. Equivalent amounts of bases are exchanged in many cases.

Two different views have been advanced to explain the facts. The older chemical view regards the process as a chemical interaction between definite acids (*e. g.*, humus acid) or complex salts (*e. g.*, silicates) and salt solutions. The other view begins with von Bemmelen, and regards it as an adsorption process. Cameron suggested (*cp.* Russell's Report) that the soil adsorbs the base more strongly than it adsorbs the acid.

The objections against the chemical view can be summarized as follows:—The extract with pure water being neutral, the soil-acids must be insoluble. The acids must be unusually strong, as they evidently decompose a neutral salt solution combining with the base, liberating the strongest known acids, like hydrochloric acid.

Evidently such acids are unknown, and it is difficult to conceive of such reactions. Regarding the exchange of bases, the difficulty lies in the assumption that the basic ion is taken up to form an insoluble salt. It is necessary to postulate the existence of insoluble salts of alkali metals in a large number of cases (*cp.* the remarks on Freundlich's theory).

That adsorption plays an important part is also evident from the works of Russell and Prescott (*J. Agric. Sci.* viii. p. 65 (1916)) on the interaction of dilute acids and phosphates present in the soil. But the view of Cameron does

not seem to be tenable. The preferential adsorption of an ion by the soil does not mean hydrolytic decomposition of the salt. It appears from the summary given by Russell that the equivalent exchange of bases lies in the way of regarding the reaction as an adsorption process (*loc. cit.* pp. 71, 75, 76). It would be apparent from the previous discussion that this, in itself, does not contradict the adsorption hypothesis.

Soil can be regarded as a complex colloidal system. It is a complex gel consisting of aluminium and other silicates, free silica, ferric hydroxide, etc. The gel is mixed with insoluble crystalloids. It also contains small quantities of adsorbed electrolytes and organic matter in indefinite and varying proportions. The gel adsorbs anions by chemical affinity. These anions may be:—

- (1) of organic acids, such as humus acid ;
- (2) of simple electrolytes like chlorides, sulphates, carbonates, etc. ;
- (3) hydroxyl ions from water.

Owing to the complex chemical nature of the gel and the enormous specific surface of gels, large quantities of anions may be adsorbed. An equivalent number of cations remain near the surface as the mobile second sheet or as electrically adsorbed. The exchange of bases is simply due to the displacement of these ions. When the displacement is quantitative equivalent amounts are exchanged. The anions primarily adsorbed or the cations in the second sheet are not of one kind. The relative numbers and chemical natures of these ions will evidently vary with the different soils.

An extract with pure water will be neutral unless the soil contains free acids. An extract with a neutral salt can only be acid when the cations displaced from the second sheet (or electrically adsorbed) contain hydrogen ions or such ions as aluminium, which hydrolyse in dilute aqueous solutions. The role of the aluminium ions in determining the acidity of the soil extract has been pointed out by Daikubara (Bull. Imp. Central Agri. Expt. Station, Tokio, ii. pp. 1-40 (1914)), and has been fully confirmed by Rice (*loc. cit.*). The function of organic acids has constituted a great objection against the adsorption hypothesis. The hydrogen ions in the second sheet have probably, in most cases, their origin in these acids. This view thus correlates the exchange of bases observed with soil with such exchanges as have been observed in the adsorption of electrolytes (*cp.* Michaelis).

That sometimes considerable quantities of bases are exchanged should be referred to the enormous surface of these

gels, and that probably the surface is saturated with anions. As crystalloids (insoluble) are also present, the type of exchange considered by Paneth (*loc. cit.*) is also possible.

It is needless to point out that in this discussion only the theoretically simple case has been considered. Complications due to simultaneous primary adsorption of different ions and their mutual displacement are not always negligible. Besides, the changes may not be restricted to the surface; formation of solid solutions, etc., are not excluded. Considering all these complex influences, it is interesting to note that most of the observed regularities correspond to the theoretically simple case.

*Adsorption of Ions in its Relation to Permeability of
Membranes and to Negative Osmosis.*

In conclusion, a few remarks will be made on the fundamental interest that a study of the adsorption of ions has for biological phenomena. Cell activity is greatly conditioned by the permeability of its "walls" or the cell-substance to the contents of the liquid with which it is in contact. The connexion between the rate of osmotic flow through membranes and even the direction of the flow, and the potential differences existing on the two sides of the membranes, has been clearly established (Girard, *C. R.* cxlvi. p. 927 (1908), and following authors: Bartell, *J. Amer. Chem. Soc.* xxxvi. p. 646 (1914); Hamburger, *Z. Phys. Chem.* xcii. p. 385 (1917)). The origin of the potential difference is generally assumed to be due to the fact that the rate of diffusion of the electrolytic ions in the membrane substances is different from that in water. That the membrane potential is due to a selective permeability of ions was first suggested by Ostwald (*Z. Phys. Chem.* vi. p. 71 (1890)); Donnan (*Z. Elektrochem.* xvii. p. 572 (1911)) has discussed the origin of the potential differences theoretically, and has given it a quantitative form based on thermodynamic considerations. In collaboration with others he has carried out a number of investigations which have established the validity of this view.

The simpler case of a potential difference between two interfaces when an immiscible liquid is placed between two aqueous solutions has also attracted a good deal of attention. The work of Loeb and his co-workers on cell-permeability and origin of the membrane potential is of fundamental importance (Loeb and Beutner, *Biochem. Zeit.* li. p. 295 (1913); Beutner, *Z. Phys. Chem.* lxxxvii. p. 385

(1914), *Z. Elektrochem.* xix. pp. 329, 473 (1913); Loeb, *J. Gen. Phys.* xx. p. 173 (1919), ii. pp. 273, 255, 387, 577, 563, 673, 659). The part played by the adsorption of ions in these phenomena is twofold. The origin of the potential is in many instances due to the adsorption of ions (*cp.* Baur, *Z. Elektrochem.* xix. p. 590 (1913); *Z. Phys. Chem.* xcii. 1916, p. 81).

Secondly, the electrostatic forces of the surface probably determine the relative permeabilities of the two ions. To this the semi-permeability of an ion can be referred.

Regarding negative osmosis, attention may be drawn to the suggestion of Freundlich (*Koll. Zeitsch.* xviii. p. 1 (1916)) that the thin walls of the membrane substance conduct electricity, and electro-osmotic flow of the liquid occurs. A necessary condition is that one ion is permeable and the other relatively impermeable. This explanation meets thermodynamical requirements, and is the only satisfactory one hitherto put forward.

In all these cases the same influences of polyvalent ions and ions of opposite charge are noticeable.

The change in the colloidal properties of the membrane is an important additional factor which has to be remembered. The influence of the electrostatic forces is unmistakable.

Physical Chemistry Department,
University College, London.

XXX. On certain Assumptions in the Quantum-Orbit Theory of Spectra. By W. M. HICKS, F.R.S.*

THE practically complete success of the quantum-orbit theory in describing all the known facts of spectra, in cases where we know experimentally that the source consists of a single nucleus and a single electron, must give assurance that the same procedure must also be capable of application to more complicated atoms than those of the hydrogen and enhanced helium types. Unfortunately, however, mathematical difficulties have so far prevented any rigorous application of the theory to definite cases, even of the next simplest atomic configuration of a single nucleus and two electrons. The attempt of Sommerfeld at an approximate solution shows, on the one hand, how hopeful we may be of a description of spectra on this basis, and at the same time how far we are at present from its

* Communicated by the Author.

achievement. In the present note I wish to illustrate this by drawing attention to certain assumptions as to actual spectral data, which have been made and which do not appear to be justified. The criticisms may not affect essential points, but they would appear to require some modification in the presentment of the theory. References will be made to Sommerfeld's 'Atombau und Spektrallinien,' 2nd edition (1921).

1. Sommerfeld (pp. 276, 506) takes a configuration of a central nucleus, surrounded by a ring of equally-spaced electrons, and at a considerable distance further out one electron revolving in a quantized orbit. On the assumption—here justified—that the ring can be treated as if the whole charge of the electrons on it were continuously distributed along it, he obtains as an approximation the same form for a sequence function (or term) p as that suggested by Ritz, viz.*:

$$p = N/\{m + \mu + \alpha p\}^2.$$

He says that this is the actual true form, as already determined by observation. This is, however, by no means the case. No form has yet been found which will fit in for all series, and indeed the form $N/(m + \mu + \alpha/m)^2$ is in general rather superior to that of Ritz. It is to be noted that the assumption made above leads to the same result as if the force to the centre depended only on forces inversely as even powers of the distance, and forces depending on odd powers—say $1/r^3$ —are excluded. It may also be noted in passing that the theory so developed applies only to the case of a single external electron and one internal ring, that is, on the usually assumed configuration of eight-electron rings, only to the spectra of the fluorine group, or the ionized rare gases, or the doubly-ionized alkalies, etc. By taking his E as $(k - s)e$ in place of ke , the formula would meet the more general case. This modification, however, would only slightly affect the order of magnitude of the quantities μ, α .

In the formula $m = n + n'$, where n, n' are respectively azimuthal and radial quantum numbers, and μ, α are functions of n and not of n' .

* As a result of successive approximation, α being small, this means for a complete approximation the form

$$p = N/\{m + \mu + \alpha/(m + \mu)^2 + \beta/(m + \mu)^4 + \dots\}^2,$$

which, as is well known, is capable of reproducing practically all cases if $\mu, \alpha, \beta \dots$ are all at disposal, and are not related necessarily to one another, as here.

It is not to be expected that the numerical values of the constants μ , α on this special theory should accord with any determined by experiment, but they should be of a suitable order of magnitude and general character. It may be interesting to test this. The expressions for the constants μ , α may be written

$$\mu = \frac{\beta}{n^3} \left\{ 1 + \frac{15}{4} \frac{\beta}{n^4} \left(1 - \frac{3}{2} \frac{k-s_k}{Z-k} \right) r^2 \right\} r^2,$$

where

$$\beta = \frac{(2\pi)^4 m^2 e^3 E(Z-k)}{4h^4} = 8.9(Z-k)(k-s_k)10^{15} r^2$$

and

$$\frac{\alpha}{\mu} = -\frac{3\pi^2 m}{2n^2 h} \left(\frac{9}{2} - \frac{Z-k}{k-s_k} \right) r^2.$$

If p be measured in wave number instead of frequency, the α must be multiplied by the velocity of light. Then

$$\frac{\alpha c}{\mu} = \frac{6.12}{n^2} \left(\frac{9}{2} - \frac{Z-k}{k-s_k} \right) 10^{10} r^2.$$

Here r denotes the radius of the internal ring in cm., Z the atomic number of the element, k the number of external electrons, and s_k depends on the mutual action of the external electrons on one of them. For Li, $Z=11$, $k=3$, $s_k=.577$, and

$$\mu = \frac{2.2}{n^3} \left(1 + \frac{4.5}{n^4} 10^{16} r^2 \right) 10^{16} r^2,$$

$$\frac{\alpha c}{\mu} = \frac{7.3}{n^2} 10^{10} r^2.$$

In actual cases, for wave numbers of about $p=10^5$, $\mu \alpha c / \mu$ lies between about .9 and .01. Hence the second equation requires $r < 10^{-7.5} > 10^{-8.5}$. Since $\mu < 1$, the first equation requires r to be about 10^{-8} , but as the second term in the bracket is determined by an approximation it must be a small fraction, whence $r < 10^{-8.5}$. The fact that both give values of the same order of magnitude, even if they cannot exactly agree, and not far from what might be expected for an 8-electron ring, is certainly satisfactory.

2. It is deduced that the different types of sequences correspond to azimuthal numbers $n=1, 2, 3, 4$, the different orders of the same type to radial quanta $n'=0, 1, \dots$. These are then co-ordinated with the s, p, d, f types because it is stated that these types have their lowest orders respectively of 1, 2, 3, 4. It is difficult to see how this statement has been arrived at, as it is quite incorrect. For the sake of

readers who may not be familiar with spectral data, it may be well to consider them here.

(*s, p.*) For the *s, p* the lowest order are :

	<i>s.</i>	<i>p.</i>		<i>s.</i>	<i>p.</i>
Rare gases	1	1			
I. { The alkalis	1	2	II. { Alkaline earths ...	2	1
{ Cu, Ag, Au.....	1	1	{ Zn, Cd, Eu, Hg...	2	1
			Group III.	2	1

If it were not for the cases of the rare gases and the Cu subgroup, the assumption might be explained by an interchange of the nature of the sequences which produce P, S series (for which in Groups I. and II. indeed there is also direct evidence). But that two groups make *s, p* both have unity for their first order is fatal.

(*d.*) The assumption of 3 as the first order for *d(m)* no doubt is based on the fact that Ritz made it in dealing with the D series in the alkalis. The denominators of the first orders in this group are comparable with 2.9, which Ritz wrote as $3 - .1$ and called the first order 3. But this procedure is inadmissible either on the side of the formula or from what we know of the constitution of the *d* sequence. In Sommerfeld's formula μ is positive, and it is only by treating the fraction as positive that we find a definite dependence of it on certain spectral constants. But even so, the first order is not 2 for all groups. The law of the first order of the *d* sequence is a quite simple and definite one, and is given on p. 188 of my recently published 'Analysis of Spectra.' It is that in each group of the periodic series, the subgroup of elements whose melting-points increase with atomic weight take as their first order $m=1$, whilst the subgroup with decreasing melting-points take $m=2$.

(*f.*) In the case of *f* the $3 + \text{fraction}$ has again clearly been written $4 - f$, and the assumption has been made that the lowest orders of the *f* type take $m=4$. But here also, for the same reasons as in *d*, the fraction must be taken as positive. In the alkalis certainly the lowest order observed is F(3), but F(2) would lie far up in the ultra-red, beyond even Paschen's longest lines. In the Cu subgroup there is evidence for $m=2$ and indications for $m=1$. The alkaline earths have $m=2$ both in triplets and doublets. In the Zn subgroup only F(3) has been observed, but F(2) would lie in the extreme ultra-red. In Group III. there is no evidence, whilst in the rare gases there are examples of F(1) and F(2).

It would thus appear that the theoretical deduction that different types depend on successive changes of azimuthal quanta by unity is not tenable.

3. In dealing with the Zeeman effect on p. 422, Sommerfeld adopts Paschen and Back's interpretation of their experiments on the Zeeman effect in the case of close multiple lines. This interpretation was based on preconceptions as to the nature of the series types in He and Li, which they investigated. I have given * reasons why this interpretation should be modified. On either interpretation, however, a consequence follows which appears difficult to explain on the quantum-orbit theory. Take, for example, the case of the helium doublet at $4\bar{7}13\text{ \AA}$. Each component in weak fields shows special Zeeman patterns. With increasing fields and consequent approximation of certain constituents from each pattern, an interaction occurs of one on the other. Such an effect can only be produced if the two patterns are produced in the same source. Hence the original components of such a doublet must be produced simultaneously in each atomic configuration, whether a magnetic field is present or not. It follows that in radiation there must be simultaneous passages of two electrons, each from its original orbit to its final one. But as the effect takes place at one operation, the total change of energy is passed on to the radiator and emitted as a single monochromatic radiation, *i. e.* no doublet. It might be suggested that the effect could be explained on the hypothesis that the magnetic field affects the mutual *possible* orbits, and that sometimes one passage occurs and sometimes the other. It is difficult to see, however, how an orbit can be modified by another supposed one which is non-existent, *i. e.* not being described at the same time.

4. This consideration does not affect evidence for the quantum theory, but will serve to illustrate a habit which is somewhat exasperating in reading the writings of many exponents of the quantum theory—viz., the picking up of small and often irrelevant points as charming results of the theory. On p. 300 ff. it is expected that each doublet separation on passage from arc to spark conditions should be magnified in a measure corresponding to the ratio $4N:N'$, and satisfaction is expressed that in data adduced from corresponding elements in the doublets of group I. and the enhanced doublets of group II. this expectation is fulfilled. The ratios of the separations are reproduced (with Hg: Au added) in the first line of the following:—

Mg.	Ca.	Sr.	Ba.	—	Zn.	Cd.	Eu.	Hg.
5.3	3.9	3.4	3.1		3.5	2.7	?	2.5
2.24	2.10	2.03	1.92		2.24	2.12	2.03	2.12

* 'Analysis of Spectra,' § 7, p. 96.

But surely these numbers show that the comparison is not justified. As is known, a correspondence actually lies between the enhanced doublets and the triplets in the same element. Thus the ratios of the doublets to the first separation of the triplets are given in the second line of figures above, where the agreement is remarkably close. In this latter case, however, the correlation is not direct. It is due to three concurrent facts: (1) ratio $4N:N$; (2) the σ multiples in the doublets and ν_1 of the triplets are very nearly the same in each element; and (3) the denominators in the doublets and triplets have nearly the same ratio in all (see below). There is, however, a close correspondence between the mantissæ of the doublets in the two groups I. and II., especially as between the alkalis and the alkaline earths, those of the latter being about double the first. Correlation is also shown between the denominators of the triplet and doublet sets in all the group II. elements. These statements are illustrated by the following data:—

II.				I.	
	Tripl.	Doubl.	Ratio.		Doubl. Ratio.
Mg	1·660	2·265	1·36	Na	2·117 2·27
Ca	1·796	2·498	1·39	K	2·235 2·12
Sr	1·880	2·611	1·39	Rb	2·292 2·09
Ba	1·957	2·735	1·39	Cs	2·361 2·03
Zn	1·559	2·098	1·31	Cu	1·869
Cd	1·641	2·144	1·30	Ag	1·892
Eu	1·648	2·190	1·32	—	—
Hg	1·653	?	—	Au	1·929

Here under II. the third column gives the ratio of the denominators; under I. the second column gives the ratio of mantissæ in II. to those in I.

On the other hand, there appears very little correlation between the σ multiples which give the separations in corresponding elements of groups I. and II. A much closer one is found between those of the triplets and doublets of the same element in II. Thus, in the following, the first line gives the ratios of the σ multiples of doublets in group I. to those of the enhanced doublet of the corresponding element in group II. The second line gives the ratios of these multiples for the first triplet separation and the enhanced doublet in each element.

Mg.	Ca.	Sr.	Ba.	Zn.	Cd.	Eu.	Hg.
·683	·779	·843	·903	·847	1·1	—	?
·691	·709	·726	·761	·789	·846	·842	?

XXXI. *On the Theory of the Characteristic Curve of a Photographic Emulsion.* (Communication No. 22 from the British Photographic Research Association Laboratory.)
By F. C. Toy, *M.Sc., F.Inst.P., F.R.P.S.* *

IN the most recent investigations on the relation between the photographic effect and the light-exposure, special plates containing only a single layer of grains have usually been employed. With such plates the photographic effect is determined by counting the percentage of grains made developable. The curve expressing the relation between this percentage (x) and the logarithm of the exposure may be called the characteristic curve of a single-layer emulsion, corresponding to the ordinary curve of a commercial emulsion, in which, instead of x , values of the density (in the photographic sense) are plotted.

In a recent paper (Phot. Jour. 1921, lxi. p. 417) the author has shown that such a curve, for a set of grains which are geometrically identical, is of the usual S-shaped type, *i. e.* a difference in size or shape does not account for the fact that all the grains do not become developable with the same exposure. Now, a set of geometrically identical grains, all in a single layer and similarly orientated to the incident light, represents the simplest possible emulsion which we can investigate experimentally. It also corresponds to the simplest theoretical case, eliminating many complicating factors which, though greatly affecting the form of the characteristic curve, have nothing to do with the primary mechanism of the photographic process. In other words, with this emulsion the curve is reduced to its "purest" form, and is determined almost solely by the photochemical process which takes place.

It is now generally believed that the primary action of light on the grains is to form in or on the surfaces of them certain "centres" or "points of infection" which act as starting-points for their reduction by the developer. This view has for some time had considerable evidence in its favour. Chapman Jones (Phot. Jour. 1911, li. p. 159) showed that by stopping development at a very early stage it is possible to get particles of silver too small to be visible microscopically, but which can be shown to be present by the colour imparted to the film, and by enlargement to visible dimensions by the deposition on them of mercury. Hodgson (Brit. Jour. Phot. 1917, p. 532) carried development a little

* Communicated by Prof. A. W. Porter, F.R.S.

further, and showed it possible to observe the silver reduced by the developer only around certain centres in the grain, and a recent paper of Svedberg's (Phot. Jour. April 1922) leaves little room for doubt that the possibility of a grain being made developable depends on the existence in it of some kind of reduction centre.

Opinion as to the nature of these centres seems at present to be divided. There are those who assert that they are formed by the light-action, and that they do not exist before exposure is made. Such, for example, is the case if the centre is really a molecule of silver halide which has lost an electron, as is believed by H. S. Allen (Phot. Journ. 1914, liv. p. 175). On the other hand, there are those who believe that the centres are actual particles other than silver halide formed in the grains during precipitation and subsequent ripening, and that these only become susceptible to the action of developer after exposure to light.

There certainly is considerable evidence to show that silver halide is not the only substance in the grains. Luppocramer (*Kolloidchemie und Photographie*) was led, as a result of his work, to the conclusion that, at any rate in the most sensitive emulsions, nuclei are present which probably consist of a colloidal solution of silver in the halide. Renwick (J. S. C. I. 1920, xxxix. No. 12, 156 T.) extends this idea, and says: "In our most highly sensitive photographic plates we are dealing with crystalline silver bromide in which, besides gelatin, some highly unstable form of colloidal silver exists in solid solution, and it is this dissolved silver which first undergoes change on exposure to light." These silver particles are negatively charged, and Renwick believes that the action of light is to discharge, and hence to coagulate into larger groups, those particles of colloidal silver which existed in the grain before exposure; it is these groups of coagulated electrically neutral particles which are the reduction centres. This view is supported by the ultra-microscopic observations of Galecki (*Koll. Zeit.* 1912, x. pp. 149-150), who showed that X-rays have a coagulating effect on the particles in gold sols; by Svedberg (*Koll. Zeit.* 1909, iv. p. 238), who has similarly shown that ultra-violet light agglomerates ultra-microns to larger aggregates; by Spear, Jones, Neave, and Shlager (J. Amer. Chem. Soc. 1921, xliii. p. 1385), who have observed the same kind of effect with colloidal platinum; and by recent experiments of Weiger and Scholler (*Sitz. Preuss. Akad. Wiss. Berlin*, 1921, pp. 641-650).

These facts are at any rate sufficient to justify an attempt to explain the relation of the number of grains changed to the light-intensity on the basis of the existence in the grains of actual particles which are not silver halide. These are not necessarily all changed to reduction centres from inactive particles by the same light-energy as they would be if they were single molecules of the halide. We shall make no assumptions as to the composition of these centres, and the theory does not depend on their being composed of colloidal silver. We shall use the term "nucleus" rather than centre to indicate the presence in the grains of actual particles before exposure.

*The Characteristic Curve of a Set of Geometrically
Identical Grains.*

Theoretical.

Our first object is to consider the case of a set of grains of identical size and shape, and to determine the relation we should expect to find between the percentage of these which are made developable and the light-intensity. The time of exposure is kept constant throughout.

If we consider a volume V of the silver halide which is very large compared with that of a single grain, we may assume that the total number of nuclei in any such volume of the emulsion is the same, though the number contained in individual grains in this volume may vary. We will define the sensitivity of a single nucleus as the minimum intensity which must be incident upon it in order to make it "active" in the presence of the developer. For a given intensity of the incident light there will be a definite number of such active nuclei in every volume V , and *they will be distributed amongst the grains entirely haphazard, according to the laws of chance. Every grain which happens to have at least one active nucleus will be developable.*

When the intensity of the light increases, more grains are changed. On any "nucleus" theory this happens because more nuclei are present, so that a single grain has a greater chance of having at least one of them. This may be explained in one of two ways. Firstly, all nuclei may have the same sensitivity, say I , but owing to the rapid absorption of light, those nuclei which are situated in the grain at some distance from the surface on which the light is incident, do not receive an intensity of I when the incident intensity is small. As the latter becomes greater, the volume of silver halide, throughout which the intensity is at least I , increases,

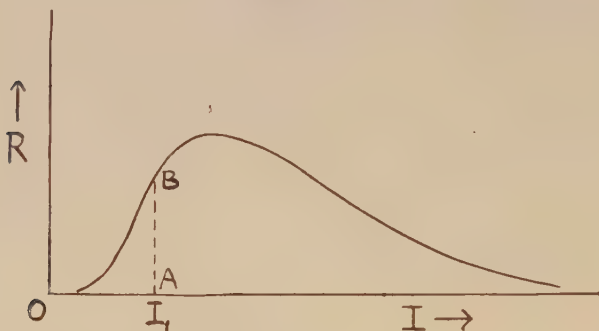
so that the number of active nuclei increases also. Secondly, the sensitivity of every nucleus may not be the same, so that as the intensity of the light is increased, nuclei become operative which are unaffected by lower intensities, and again the total number of active nuclei increases with the intensity.

We will consider only the case of grains in the form of thin plates as they occur in high-speed emulsions. Eggert and Noddack (*Preuss. Akad. Wiss. Berlin. Ber.* 1921, xxxix. p. 631) have recently measured photometrically the fraction of the incident light which is absorbed by an ordinary commercial photographic plate, and have found it to vary with the different plates from about 4 to 12 per cent. for violet light, for which the amount of light absorbed is near the maximum. Now, these plates contain several layers of grains, so that a very extreme upper limit to the fraction of light absorbed by a single grain is, say, 20 per cent. Thus, if there is an increase in the incident intensity of the order of 20 per cent., the intensity of the light transmitted through a grain will be equal to the intensity incident before the increase took place. Thus, if all nuclei are equally sensitive, a change in the incident intensity of the order of 20 per cent. will cause a difference in the number of active nuclei from zero to some fixed maximum, so that the characteristic curve can only function over a range of intensity such that the ratio of its extremes is of the order of 1.2:1. As will be shown later, for the steepest characteristic curve plotted this ratio is about 25 times as much as this, so that as an appreciable factor in determining the increase of nuclei with intensity the first assumption is untenable. We have, therefore, to assume that all the nuclei are not equally sensitive.

Since these nuclei are all formed in the same emulsion, most of them will have a sensitivity near the average value for the whole, and there will be a few which are very sensitive and a few which are very insensitive. There will be none which will respond to zero intensity, and none so insensitive that it takes an infinite intensity to affect them. We therefore expect the curve showing the relative number of nuclei R having any given sensitivity I to be of the general form shown in fig. 1. The exact mathematical form of this curve is immaterial at present, but it will be similar in general form to that obtained by Clerk Maxwell for the distribution of velocities between the molecules of a gas. By similar reasoning to his, the number of nuclei (N_1) which

have sensitivities between zero and I_1 (which is the number operative when the intensity of the light is I_1) is given by

Fig. 1.



the area OAB, *i. e.*

$$N_1 = \int_0^{I_1} f(I) dI, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

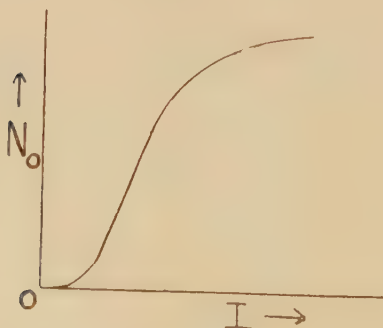
where $f(I)$ gives the values of the ordinates in terms of I ; or if N_0 is the average number of nuclei per grain and a the number of grains in volume V ,

$$N_0 = \frac{1}{a} \int_0^{I_1} f(I) \cdot dI. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The total number of nuclei is given by

$$N = \int_0^{\infty} f(I) \cdot dI.$$

Fig. 2.



The curve showing the relation between N_0 and I , shown in fig. 2, is characterized by its unsymmetrical-shaped S form.

When the a grains in the volume V of silver halide are subjected to an intensity I_1 , every grain which happens to have at least one of these N_1 nuclei will be made developable. We have, therefore, to find the chance of a grain containing at least one of the N_1 nuclei when they are distributed haphazard amongst a grains. This can easily be obtained from the theory of probability.

If p denotes the very small probability that an event will happen on a single trial, the probability P_r that it will happen r times in a very great number, say n trials, is (Mellor, 'Higher Mathematics,' p. 502)

$$P_r = (np)^r \cdot e^{-np} / r! \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Let the volume of a single grain be v , then since the volume of every grain is the same the total volume V is av . Let p be the very small probability that a volume dv will contain a nucleus, then

$$p = N_1 \cdot dv / av \quad . \quad . \quad . \quad . \quad . \quad (4)$$

To obtain the probability of the volume v containing a nucleus, we may suppose each dv to be a trial, so that the number of trials n is

$$n = v / dv \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Therefore the value of np in equation (3) is N_1/a , which is equal to N_0 . If in this number of trials the event (i. e. v containing a nucleus) happens once, a grain will contain one nucleus; if it happens r times it will contain r nuclei, so that from (3), (4), and (5) we see that the probability of a grain containing r nuclei is

$$P_r = (N_0)^r e^{-N_0} / r! \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which is the same equation as was obtained independently and first published by Svedberg. The probability of a grain containing no nuclei is the value of this expression when $r=0$, i. e.

$$P_0 = e^{-N_0}$$

Now, since it is certain that a grain must contain either zero or at least one nucleus, the probability P_1 that a grain will have at least one is

$$P_1 = 1 - e^{-N_0} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

But if x/a is the fraction of grains which are changed,

$$P_1 = x/a;$$

$$\therefore x/a = 1 - e^{-N_0},$$

or, denoting $\log a/(a-x)$ by A , we have

$$A = N_0.$$

Thus the same form of curve should be obtained when N_0 is plotted against the intensity as is obtained when A is plotted against the same variable. The form of this curve should be an unsymmetrical S, as shown in fig. 2.

Experimental.

The first experiment carried out was to determine the relation between A and the light-intensity I for a set of geometrically identical grains, every grain counted being measured, as described in a previous paper (Phot. Jour. 1921, lxi. p. 417).

TABLE I.

Cross-section of grain = $0.98\mu^2$.

Log I (relative).	x .	x (curve values.)	A .	Log I.	x .	x (curve values.)	A .
0	92.0	91.5	2.45	-0.893	47.7	46.6	0.62
-0.162	89.5	90.0	2.30	-1.215	5.2	5.2	0.05
-0.310	87.7	87.0	2.04	-1.487	0.0	0.0	0.00
-0.572	74.8	75.0	1.39	-1.788	0.0	0.0	0.00

In the first two columns of Table I. are shown the values of $\log I$ and x determined experimentally by exposure behind a neutral wedge, and these are plotted in fig. 3. The values of x given in column 3 are read off the curve in fig. 3, and it is these values which are used in calculating A in column 4. This is the best way of obtaining the A values, since when x is large a very small error in its determination means a very large error in A . The A, I curve, shown by the solid line in fig. 4, is exactly as predicted by the theory.

We must note here that this is not in agreement with the results of Slade and Higson (Proc. Roy. Soc. 1921, A, xcvi. p. 154) and a previous experiment of the author (ibid. 1921, c. p. 109) to confirm their result. Slade and Higson stated that the relation between A and I can be expressed by the equation

$$A = \alpha I(1 - e^{-\beta I}),$$

where α and β are constants. A comparison of the form of this curve (fig. 5) and the curve in fig. 4 shows a difference

Fig. 3.

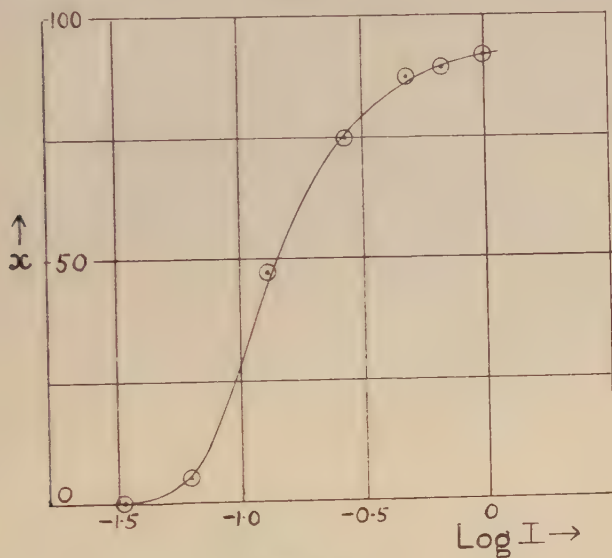
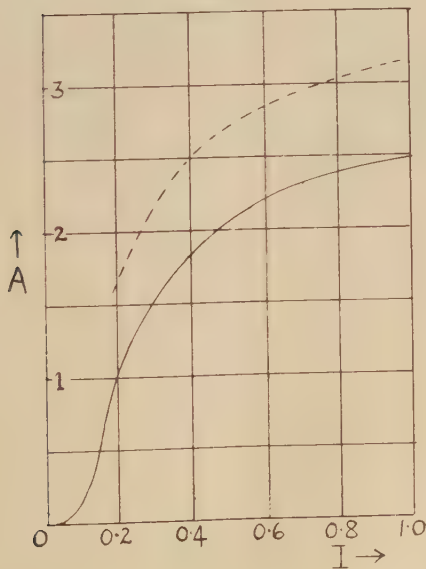
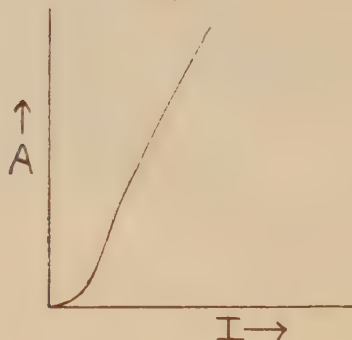


Fig. 4.



when I is large, but this can be explained. Firstly, the grains used in Slade and Higson's experiments were not all of one size, the variation being about 30 times that in the present case. Secondly, the best curve given in Slade and Higson's paper has actually the same form as that in fig. 4 if equal weight is given to each point plotted. Also, in the author's confirmatory experiment, the main point was to show that at low intensities A varied, at any rate approximately, as I^2 ; at high intensities the work was not nearly as accurate

Fig. 5.



as in the present case. To be certain of the form of the curve in fig. 4 the upper part of it was plotted for another size of grain, and that the same result was obtained is shown by the dotted line.

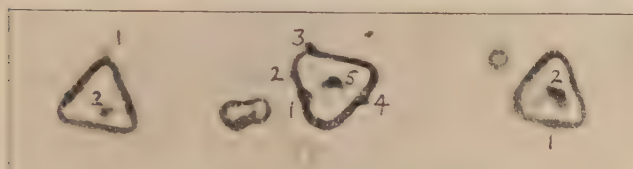
The position of a nucleus can be detected by Hodgson's method of partial development of the exposed grains (*ibid.*). The developer used was made up as follows:—

200 c.c. saturated Na_2SO_3 ,
 8 c.c. 10 per cent. KBr ,
 0.3 gm. Amidol.

This is a weak, slow developer, and is best for this purpose because there is a bigger latitude than if the developer is strong in the time of development necessary to render the position of the nuclei visible and yet distinct from one another. The best development time was found by trial and examination of the grains under the microscope. After exposure the plate was plunged into the developer for a known time, then quickly and thoroughly washed, and dried without fixing. The flat triangular grains used were so thin that the silver deposit was visible without dissolving away

the silver bromide. In fig. 6 are given some examples of grains in which these nuclei appear: they are formed more on the edges of the grains than anywhere else, though quite a number appear either inside or on the flat surfaces.

Fig. 6.



Positions of nuclei numbered.

The next experiment was to show if equation (6) holds good. A plate was exposed to a uniform intensity, partially developed, and the number of nuclei occurring on each of 150 grains was counted. Hence the average number per grain was known and also the number of grains having 0, 1, 2, 3, etc. nuclei each.

In Table II. are given the theoretical and observed values of P_r for two equal-sized sets of grains, in one and the same emulsion, having widely different values of N_0 .

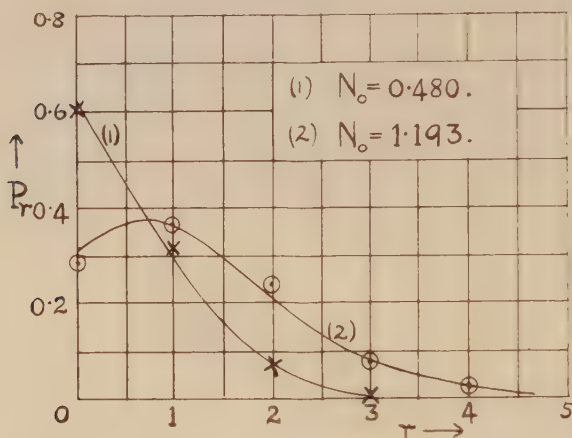
TABLE II.

$N_0=0.480.$				$N_0=1.193.$			
Value of r .	No. grains having r nuclei.	Probability = P_r .		Value of r .	No. grains having r nuclei.	Probability = P_r .	
		Obs.	Calc.			Obs.	Calc.
0	91	0.607	0.619	0	43	0.287	0.303
1	47	0.313	0.297	1	55	0.367	0.362
2	11	0.073	0.071	2	36	0.240	0.216
3	1	0.007	0.001	3	12	0.080	0.086
4	0	0.000	0.001	4	4	0.027	0.026

The observed values of P_r were determined by the fact that the probability of a grain having r nuclei is equal to the fraction obtained by dividing the number of grains which have r nuclei by the total number, *i. e.* 150. In fig. 7 the theoretical values are represented by the smooth curves, and

those observed by the plotted points. The agreement is very good, and proves the validity of equation (6) in the case of a fast emulsion.

Fig. 7.



To find the relation between the average number of nuclei per grain and the intensity, a plate was exposed behind a step wedge and partially developed. The size of grain selected was the same as used for determining the A, I curve in fig. 4, the plate being exposed for approximately the same time behind the same wedge. At each intensity (I) the total number of nuclei on 200 grains was counted (except at $I=0.044$, where 100 grains were considered sufficient), and hence the average number per grain found. The values are given in Table III., and it will be seen that the curve in fig. 8 is of the same general form as the A, I curve in fig. 4, as is predicted by the theory.

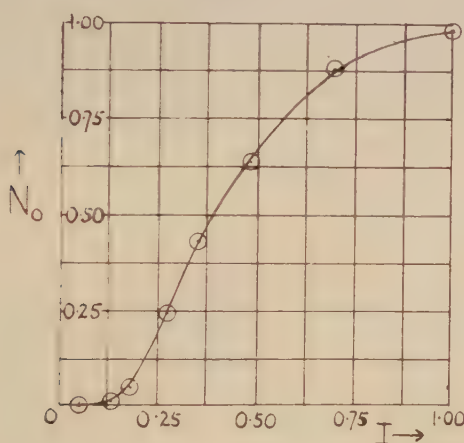
TABLE III.

Cross-section of grain = $0.98\mu^2$.

I .	N_0 .	I .	N_0 .
1.000	0.98	0.270	0.24
0.689	0.88	0.180	0.05
0.490	0.63	0.128	0.02
0.356	0.43	0.044	0.00

The highest value of N_0 is about 1, which corresponds to less than 70 per cent. of grains changed, whereas actually the percentage changed corresponding to this value of N_0 was about 90. This is because the partial development has not been sufficient to show up all the nuclei, and it is very difficult to do this, since before this stage is reached, nuclei which initially were distinguishable from one another have grown together into a single mass of silver. It is, however, very unlikely that even if every nucleus could be observed the general form of the curve in fig. 8 would be changed.

Fig. 8.



The most natural assumption to make is that longer development would merely result in an increase of the number of visible nuclei in proportion to the number already observable, and that this is the case is shown by the following experiment :—Two plates were given the same exposure under the wedge and partially developed, one for 15, and the other for 18 seconds. The values of N_0 were then found for widely different intensities, with the following results :—

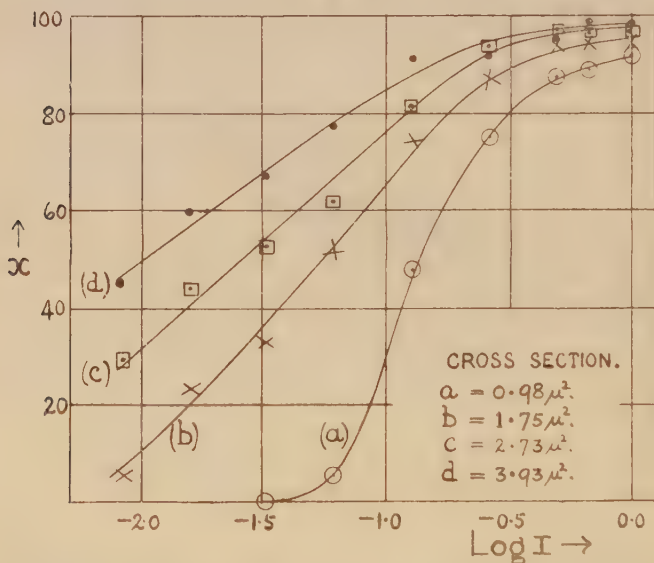
- (1) $I = 1.00$, N_0 for 15 seconds development = 0.613, N_0 for 18 seconds = 0.980, whence $(N_0)_{18}/(N_0)_{15} = 1.59$.
- (2) $I = 0.27$, $(N_0)_{15} = 0.153$, $(N_0)_{18} = 0.240$, whence $(N_0)_{18}/(N_0)_{15} = 1.57$; so that this ratio is practically constant, and the general form of the curve is independent of the development.

Variation of Grain Size.

Experimental.

It will be convenient to deal first with the experimental curves. When the values of x were being found for the curve in fig. 4, the corresponding values for three larger sizes of grain were determined at the same time and in the same way. The characteristic curves for the four sizes are shown in fig. 9.

Fig. 9.



The important points in regard to these curves are that for one and the same emulsion:—(1) a set of large grains is more sensitive than a set of small ones, which confirms Svedberg and Anderson's result (Phot. Jour. 1921, lxi. p. 325); (2) the characteristic curve for small grains has a greater maximum slope than that for large ones, *i. e.*, the ratio of the intensity which just changes all the grains to that which just causes the smallest possible change is larger the larger the grain size. As will be seen from the figure, the logarithm of this ratio for the smallest size grain is about 1.5, which is equal to an intensity ratio of 30:1, whilst for the largest size a ratio of 100:1 is necessary to give half the curve.

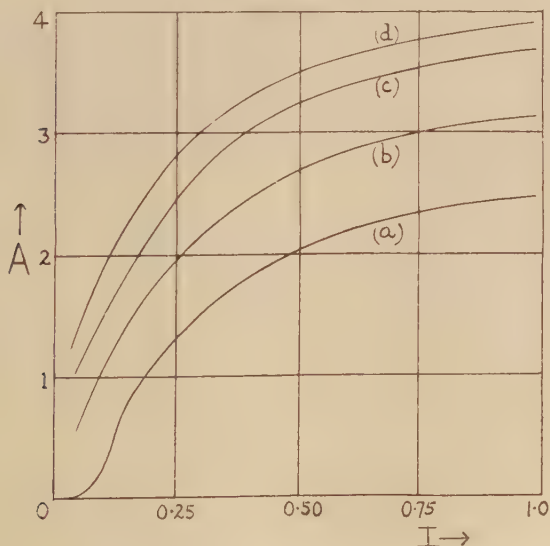
In Table IV. are given values of x , as read off the experi-

mental curves in fig. 9, corresponding to known relative intensities, and in the third column the values of A are

TABLE IV.
Cross-section of (a) = $0.98\mu^2$,
 (b) = $1.75\mu^2$,
 (c) = $2.73\mu^2$,
 (d) = $3.93\mu^2$.

Relative Intensity.	x (curve values).				A.			
	(a).	(b).	(c).	(d).	(a).	(b).	(c).	(d).
1.000	91.5	95.8	97.5	98.0	2.45	3.16	3.70	3.91
0.689	90.0	94.5	96.8	97.8	2.30	2.91	3.45	3.80
0.490	87.0	93.0	96.0	97.0	2.04	2.66	3.22	3.51
0.270	75.0	87.6	92.5	94.5	1.39	2.08	2.60	2.90
0.128	46.0	73.0	81.0	88.5	0.62	1.31	1.66	2.16
0.061	5.2	52.5	66.6	78.0	0.05	0.74	1.10	1.51
0.033	0.0	36.0	54.0	67.6	0.00	0.45	0.78	1.12
0.016	0.0	20.7	40.5	57.0	0.00	0.22	0.52	0.84
0.008	0.0	7.0	28.5	46.5	0.00	0.07	0.33	0.62

Fig. 10.



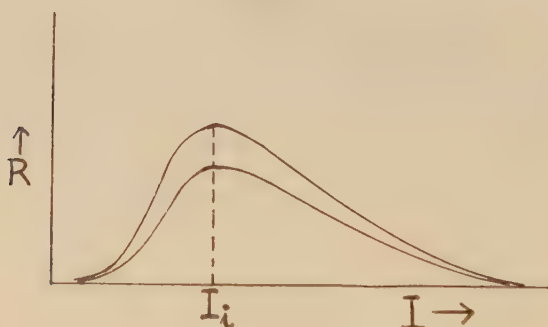
calculated. The A, I curves for the four sizes of grains are given in fig. 10.

Theoretical.

Consider what is the effect of a variation in grain size on the nuclei distribution curve shown in fig. 1.

We will first assume that the sensitivity of a nucleus is quite independent of the size of the grain in which it chances to be, *i. e.* once a nucleus is formed in a grain, its sensitivity does not change as the grain grows. This is apparently Svedberg's assumption, for he says: "the small and the larger grains in one and the same emulsion are built up of the same kind of light-sensitive material—just as if they were fragments of different size from one homogeneous silver bromide crystal." If this is the case, then the only result of increasing the size of grain is to increase the total number of nuclei, and these will be distributed amongst the different sensitivities in the same proportion as before. This is shown in fig. 11, where the distribution curves for two sizes of

Fig. 11.

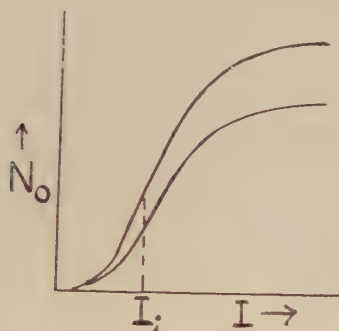


grain are given. We have made no assumption regarding the relation between total number of nuclei and grain size except that large grains have more than small ones.

The curves relating I and N_0 (average number of nuclei per grain) which will be obtained from distribution curves such as those in fig. 11 are shown in fig. 12. We have already shown that the N_0, I curve is identical in form with the A, I curve, so that those in figs. 12 and 10 should be of the same form. As a matter of fact, there is a striking difference. The experimental curves in fig. 10 lie practically parallel to one another at the higher intensities, and the point of inflexion (which corresponds to the maximum ordinate in the nuclei distribution curves in fig. 11) moves towards the origin as the grain size increases. In curves (b), (c), and (d), fig. 10, which are for exceedingly sensitive grains, the point

of inflexion has moved so near the origin that the part of the curve to the left of this point does not show on the scale to which the curves are plotted. On the other hand, the theoretical curves in fig. 12 are characterized by the fact

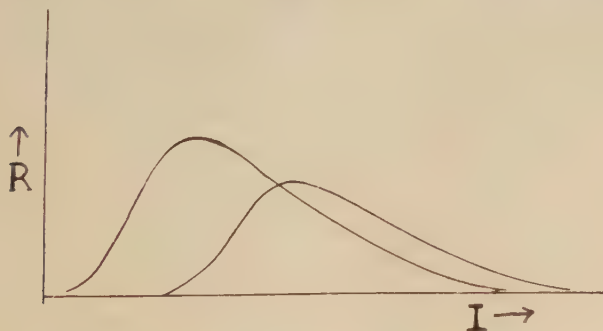
Fig. 12.



that the ratio of the ordinates for different sizes of grain is independent of the intensity, and the value of I at the points of inflexion, I_i and the average sensitivity do not change as the grain size is varied. Thus we cannot explain the effect of a variation of grain size on Svedberg's assumption.

Now let us assume that the sensitivity of a nucleus depends on the size of the grain in which it is contained, and that if

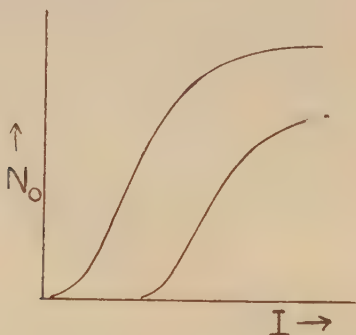
Fig. 13.



it is in a large grain it is more sensitive than it would have been in a small one. The effect of this on the distribution curve for the larger grain in fig. 11 is to shift it bodily nearer the zero, thus decreasing the value of I_i and increasing the average sensitivity, as in fig. 13. The N_0I curves

plotted from these distribution curves are shown in fig. 14, and it will be seen that they are similar to the experimental curves in fig. 10. The reason why, for *very* sensitive grains, the lower half of the S-shaped curve appears to vanish (*b*), (*c*), and (*d*), fig. 10, is that the value of I_i is very nearly zero, but it would be shown if the points were plotted on a bigger scale.

Fig. 14.



The evidence thus points to there being two reasons why large grains are more sensitive than small ones. Firstly, there are more nuclei present in the larger grains, so that a single grain has a greater chance of having at least one; and secondly, the average sensitivity of the nuclei increases with the size of grain.

Svedberg in his most recent paper (*ibid.*) discusses the relation between the average number of nuclei per grain and the grain size. He says:—"The rapidity of the increase of the average number of nuclei per grain N_0 with size of grain would depend on two factors: the ability of the developer to penetrate into the grain, and the homogeneity of the field of light in the grain. If the developer is not able to get into the interior of the grain, but only attacks the surface layer, then N_0 would mean the number of centres in that surface layer, and therefore would increase in approximate proportion to the grain surface even in cases where the field of light in the grain was not homogeneous (because of strong light absorption). On the other hand, if the developer is to penetrate the grain, N_0 would depend upon the field of light in the grain. If the absorption of light were feeble, N_0 would increase in proportion to the volume of the grain; if the absorption were very strong, N_0 would increase approximately proportionally to the cross-section of the grain." Later in

the paper he compares the variation of N_0 with grain size for grains which have been exposed to light with the variation when the exposure is to X-rays, and suggests certain deductions as regards the absorption of light and X-rays by the silver halide from the difference which he finds.

Now, from fig. 10 we see (since $A=N_0$) that the manner in which N_0 varies with grain size depends on the intensity to which the grains have been exposed; we can select an intensity such that N_0 varies in almost any manner we please. Thus, unless the difference between Svedberg's results and those found here is due to the different emulsion used, there seems to be no justification for making deductions from the relation which is found between N_0 and the size of grain at one fixed arbitrary exposure.

The theory which has been advanced here is capable of explaining an important fact which appears quite inexplicable on such a theory as Allen's (*ibid.*). It is well known that the sensitivities of the grains in an emulsion depend to a great extent on the conditions of precipitation and ripening; and that, in different emulsions, sets of equal-sized grains may have quite different sensitivities, and even different maximum slopes for their characteristic curves. If, as Allen suggests, the nucleus is really a simple molecule of silver halide which has lost an electron, its characteristics will be the same whatever the emulsion, and it is difficult to see why grains in one emulsion should be more sensitive than those of the same size in any other emulsion. If, however, the nucleus is not silver halide, it is very probable that the conditions of precipitation and ripening do play an important part in determining its characteristics.

Thus, on Renwick's theory, the condition of the colloidal silver which is produced will certainly depend on such factors as the kind of gelatin, conditions and time of ripening, etc., and the ease with which colloidal silver particles can be coagulated will be affected by the amount of gelatin present, since this is a protective colloid. The great difficulty in accepting Renwick's theory as it stands is this:—It is known that an unprotected silver sol is very stable to the action of light. Therefore, if a protective colloid is present, it will be still more difficult to effect its coagulation and precipitation by light, whereas in the case of our most sensitive silver halide grains the energy necessary to make them developable is exceedingly small.

Lüppo-Cramer (*ibid.*) believes that the mechanism of the formation of the latent image is not the same for the most sensitive and very insensitive emulsions, and he claims that

this is supported by his experiments. He found that the sensitivity of a very fast emulsion was decreased considerably by treatment with chromic acid, but that the sensitivity of a very slow emulsion remained unchanged. He explained this by the existence on the surface of the sensitive grains of colloidal silver, formed during the ripening process, which was not present in the insensitive grains, and which was removed by the chromic acid.

It is very difficult to imagine that the fundamental light action varies with the kind of emulsion, and that considering a whole series of emulsions, from the most sensitive to the most insensitive, there is a transition region where an entire change of mechanism takes place. Strong evidence against Lüppo-Cramer's view is that Svedberg (*ibid.*) has shown that in one of the slowest emulsions the reduction centres are distributed amongst the different grains according to the same law as has been shown here to hold for their distribution in the case of one of the fastest commercial emulsions. This is in favour of the view that for all kinds of emulsions the process of the formation of the latent image is the same.

The existence of this chance distribution of developable "centres" in the grains does not conclusively prove that they are the kind we have considered in this paper, and there are at least three other possibilities. Assuming a discrete structure of the radiation, the centres may, as suggested by some, be the points of impact of light quanta on the grains, but the fact that the majority of these centres are located on the *edges* of the grain is strongly against this view. Also within the crystal there may be a chance concentration of the light energy at certain points, and both these possibilities are being tested in this laboratory. Again, this chance distribution may be due merely to the fact that the grain as a whole is changed by the light, but the developer reaches some points of it sooner than others. If this is so, there appears to be no reason why the average number of centres per grain, considering only developable grains, should increase, as it does, in a regular manner with the light intensity. The author believes that the evidence so far obtained is mainly in support of the theory discussed in this paper.

In conclusion, the author wishes to express his thanks to Dr. T. Slater Price, Director of Research of the British Photographic Research Association for much valuable criticism and advice.

Summary.

A theory is advanced which explains the relation found experimentally between the number of geometrically identical silver halide grains made developable and the light intensity. It is assumed that there exist in the grains particles which are not silver halide, and which are formed during precipitation and subsequent ripening. With any normal exposure (*i. e.* one which gives a value between 0 and 100 for the percentage of developable grains), it is these particles which form the reduction nuclei, the only action of the light being to change their condition in such a way that they become susceptible to the action of the developer. Each nucleus does not necessarily require the same intensity to change it. The nuclei are scattered haphazard amongst the grains according to the laws of chance, and only grains which have at least one will be developable. The sensitivity of a grain is the sensitivity of its most sensitive nucleus.

The effect of a variation of grain size is explained, and it is shown that Svedberg's assumption regarding the similarity of the light-sensitive material in large and small grains is not in agreement with the experimental facts in the case of a fast emulsion.

XXXII. *On the Stark Effect for Strong Electric Fields.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

MY attention has been drawn to the results of experiments by Takamine and Kokubu* in which an effect of the nature indicated in a recently published paper† of mine was detected, namely, a shift of the central line in the perpendicular component of H_γ in a strong electric field. Before comparing the experimental amount of this shift with the theoretical value it would have on the Quantum theory of spectral lines, it is necessary, however, to point out a slip in my paper referred to above: thus on p. 945 a term is missing from the value of the contour integral (4), instead of (6) the full value should be

$$2\pi i \left\{ \sqrt{C} + \frac{B}{\sqrt{A}} + \frac{D}{4A^{3/2}} \left(\frac{3B^2}{A} - C \right) - \frac{5BD^2}{16A^{7/2}} \left(3C - \frac{7B^2}{A} \right) \right\}.$$

* "The Effect of an Electric Field on the Spectrum Lines of Hydrogen," Part III. *Memoirs of the College of Science, Kyoto Imperial University*, vol. iii. p. 271 (1919).

† *Phil. Mag.* xliii. May 1922, p. 943; this will be referred to freely.

Consequently the third term on the right-hand side of equation (25) p. 948 should be

$$+ \frac{h^5 F^2}{1024 \pi^6 E^4 m_0^3 e^2} \{N'(n) - N'(m)\}, \quad \dots \quad (i.)$$

where N' is now given by

$$N'(n) = (n_1 + n_2 + n_3)^4 \left\{ 35(n_1 + n_2 + n_3)^2 - 15n_3^2 - 21(n_2 - n_1)^2 - 6 \frac{N(n)}{n_1 + n_2 + n_3} \right\},$$

$N(n)$ being still given by equation (10). In view of the identity

$$\begin{aligned} N(n) &= (2n_1 + n_3)(6n_2^2 + 6n_2n_3 + n_3^2) \\ &\quad + (2n_2 + n_3)(6n_1^2 + 6n_1n_3 + n_3^2) \\ &\equiv 3(n_1 + n_2 + n_3)^3 - 3(n_1 + n_2 + n_3)(n_2 - n_1)^2 \\ &\quad - n_3^2(n_1 + n_2 + n_3), \end{aligned}$$

N' can be reduced to the form

$$N'(n) = (n_1 + n_2 + n_3)^4 \{ 17(n_1 + n_2 + n_3)^2 - 9n_3^2 - 3(n_2 - n_1)^2 \}, \quad \dots \quad (ii.)$$

which shows in conjunction with (i.) that *the remarks in the paper about the symmetry of the components are not affected by this correction.* In order to calculate the amount of shift of the middle n -component of H_γ we observe that this component can arise from any of three possible transitions corresponding to

$$(m_3, m_2, m_1; n_3, n_2, n_1)$$

$$= (3, 1, 1; 2, 0, 0) \text{ or } (1, 2, 2; 2, 0, 0) \text{ or } (1, 2, 2; 0, 1, 1)$$

respectively, the values of $\{N'(n) - N'(m)\}$ corresponding to these combinations being -2.14×10^5 , -2.59×10^5 , and again -2.59×10^5 respectively. And on substituting the values of the universal constants in (i.) for hydrogen ($E=e$) the following expression is obtained for the wave-length shift

$$\Delta\lambda = -\frac{\lambda^2}{c} \Delta\nu = -1.42 \frac{\lambda^2 F^2}{c} \{N'(n) - N'(m)\}.$$

This gives for H_γ ($\lambda = 4.34 \times 10^{-5}$) and the value of F used by Takamine and Kokubu*, namely,

$$F = 4.33 \times 10^2 \text{ c.g.s. e.s. units } [= 1.3 \times 10^5 \text{ volt} \times \text{cm.}^{-1}],$$

$$\Delta\lambda = .36 \text{ \AA} \text{ or } .43 \text{ \AA} \text{ respectively.}$$

The experimental value observed by Takamine and Kokubu is about 1 \AA , which is larger than that predicted by the Quantum theory. It is, however, possible that part of the experimental shift is due to a Doppler effect, and in any case the experiments could hardly be considered accurate enough to exclude a possible experimental error of what is only about $\frac{1}{2}$ an Angström unit. On the other hand, the *photographs of the shift* [plate ii. fig. 1] *point decidedly to a general displacement of all the components in the direction predicted by the theory*, namely towards the red, and may be taken as corroborative of at least this qualitative aspect of it. It is seen from (i.) and (ii.) that this lack of symmetry in a strong field would be expected on theoretical grounds to be more pronounced for the higher members of the Balmer Series (*e.g.* H_3 or H_4), and it would be highly desirable to obtain measurements relating to these lines as a further test for the quantitative aspect of the theory.

In conclusion I wish to thank Mr. W. E. Curtis for drawing my attention to the experimental results already referred to.

King's College, London,
May 12th, 1922.

Yours faithfully,
A. M. MOSHARRAFA.

XXXIII. *On the Damping Coefficients of the Oscillations in Three-Coupled Electric Circuits.* By E. TAKAGISHI, *Electro-technical Laboratory, Department of Communications, Tokyo, Japan*†.

THOUGH the importance of the problem of three-coupled electric circuits has arisen with reference to radio-telegraphy, it does not seem to have been attacked with any great amount of attention except by B. Mackū, E. Bellini, and very recently L. C. Jackson‡. The valuable paper of the latter made me feel very much interested, especially as it will make an important contribution to radio fields, but

* *L. c.*

† Communicated by the Author.

‡ Phil. Mag. vol. xlii. No. 247, July 1921, p. 35.

unfortunately I found there slight errors concerning the damping coefficients of the circuits.*

Now, let us proceed to correct them, using the same notation and abbreviations for the sake of simplicity. Comparing coefficients in the equations (5) and (6) in his original paper, we obtain, instead of (7),

$$\begin{aligned}
 & -2(q+r+s) \\
 & \quad = (R_1 L_2 L_3 + L_1 R_2 L_3 + L_1 L_2 R_3 \\
 & \quad \quad - R_1 M_{23}^2 - R_2 M_{31}^2 - R_3 M_{12}^2) \div D, \quad . \quad (i.) \\
 & -(\omega_1^2 + \omega_2^2 + \omega_3^2) \\
 & \quad = \left\{ \frac{L_1 L_2 - M_{12}^2}{C_3} + \frac{L_2 L_3 - M_{23}^2}{C_1} + \frac{L_3 L_1 - M_{31}^2}{C_2} \right. \\
 & \quad \quad \left. + L_1 R_2 R_3 + R_1 L_2 R_3 + R_1 R_2 L_3 \right\} \div D, \quad . \quad (ii.) \\
 & -2\{\omega_1^2(r+s) + \omega_2^2(s+q) + \omega_3^2(q+r)\} \\
 & \quad = \left\{ \frac{R_1 L_2 + L_1 R_2}{C_3} + \frac{R_2 L_3 + L_2 R_3}{C_1} + \frac{R_3 L_1 + L_3 R_1}{C_2} \right. \\
 & \quad \quad \left. + R_1 R_2 R_3 \right\} \div D, \quad . \quad (iii.) \\
 & -(\omega_1^2 \omega_2^2 + \omega_2^2 \omega_3^2 + \omega_3^2 \omega_1^2) \\
 & \quad = \left(\frac{L_1}{C_2 C_3} + \frac{L_2}{C_1 C_3} + \frac{L_3}{C_1 C_2} \right. \\
 & \quad \quad \left. + \frac{R_1 R_2}{C_3} + \frac{R_2 R_3}{C_1} + \frac{R_3 R_1}{C_2} \right) \div D, \quad . \quad (iv.) \\
 & -2(\omega_1^2 \omega_2^2 s + \omega_2^2 \omega_3^2 q + \omega_3^2 \omega_1^2 r) \\
 & \quad = \left(\frac{R_1}{C_2 C_3} + \frac{R_2}{C_1 C_3} + \frac{R_3}{C_1 C_2} \right) \div D, \quad . \quad . \quad . \quad . \quad (v.) \\
 & -\omega_1^2 \omega_2^2 \omega_3^2 \\
 & \quad = \frac{1}{C_1 C_2 C_3} \div D, \quad . \quad . \quad . \quad . \quad . \quad . \quad (vi.)
 \end{aligned}
 \tag{7'}$$

where

$$\begin{aligned}
 D = & 2M_{12} M_{23} M_{31} - L_1 L_2 L_3 \\
 & + L_1 M_{23}^2 + L_2 M_{31}^2 + L_3 M_{12}^2 \quad . \quad (vii.)
 \end{aligned}$$

From equations (7') ii., iv., vi., vii. we obtain the same equation for ω_2 as (8) and (9) in his original paper. For the damping coefficients q , r , and s , however, we find the following values, different from those in (10).

Now, making use of the abbreviations given below and in the original paper, we get the following equation :

$$\begin{aligned} -2(q+r+s) &= \frac{A}{X}, \\ -2\{q(\omega_2^2 + \omega_3^2) + r(\omega_3^2 + \omega_1^2) + s(\omega_1^2 + \omega_2^2)\} &= \frac{B}{X}, \\ -2\{\omega_2^2 \omega_3^2 q + \omega_3^2 \omega_1^2 r + \omega_1^2 \omega_2^2 s\} &= \frac{C}{X}, \end{aligned}$$

where

$$\begin{aligned} A &= k_1(1 - \beta^2) + k_2(1 - \gamma^2) + k_3(1 - \alpha^2), \\ B &= n^2(k_1 + k_2) + l^2(k_2 + k_3) + m^2(k_1 + k_3) + k_1 k_2 k_3, \\ C &= k_1 m^2 n^2 + k_2 l^2 n^2 + k_3 l^2 m^2, \\ X &= -(1 - \alpha^2 - \beta^2 - \gamma^2 - 2\alpha\beta\gamma). \end{aligned}$$

Solving these simultaneous equations, we have

$$\begin{aligned} q &= \frac{Q}{Y}, \\ r &= \frac{R}{Y}, \\ s &= \frac{S}{Y}, \end{aligned}$$

in which

$$\begin{aligned} Q &= \begin{vmatrix} \frac{A}{X} & -2 & -2 \\ \frac{B}{X} & -2(\omega_3^2 + \omega_1^2) & -2(\omega_1^2 + \omega_2^2) \\ \frac{C}{X} & -2(\omega_3^2 \omega_1^2) & -2(\omega_1^2 \omega_2^2) \end{vmatrix} = \frac{4}{X} \begin{vmatrix} A & 1 & 1 \\ B & (\omega_3^2 + \omega_1^2) & (\omega_1^2 + \omega_2^2) \\ C & \omega_3^2 \omega_1^2 & \omega_1^2 \omega_2^2 \end{vmatrix} \\ &= \frac{4}{X} (\omega_2^2 - \omega_3^2) \{A\omega_1^4 - B\omega_1^2 + C\}, \end{aligned}$$

similarly

$$R = \frac{4}{X} (\omega_3^2 - \omega_1^2) \{4\omega_2^4 - B\omega_2^2 + C\},$$

$$S = \frac{4}{X} (\omega_1^2 - \omega_2^2) \{4\omega_3^4 - B\omega_3^2 + C\},$$

and

$$Y = 8(\omega_1^2 - \omega_2^2)(\omega_2^2 - \omega_3^2)(\omega_3^2 - \omega_1^2)$$

That is,

$$\begin{aligned}
 q &= [\{ k_1 m^2 n^2 + k_2 n^2 l^2 + k_3 l^2 m^2 \} - \omega_1^2 \{ l^2 (k_2 + k_3) + m^2 (k_3 + k_1) \\
 &\quad + n^2 (k_1 + k_2) + k_1 k_2 k_3 \} + \omega_1^4 \{ k_1 (1 - \beta^2) + k_2 (1 - \gamma^2) \\
 &\quad + k_3 (1 - \alpha^2) \}] \\
 &\quad \div 2 (1 - \alpha^2 - \beta^2 - \gamma^2 - 2\alpha\beta\gamma) (\omega_1^2 - \omega_2^2) (\omega_1^2 - \omega_3^2), \\
 r &= [\{ k_1 m^2 n^2 + k_2 n^2 l^2 + k_3 l^2 m^2 \} - \omega_2^2 \{ l^2 (k_2 + k_3) + m^2 (k_3 + k_1) \\
 &\quad + n^2 (k_1 + k_2) + k_1 k_2 k_3 \} + \omega_2^4 \{ k_1 (1 - \beta^2) + k_2 (1 - \gamma^2) \\
 &\quad + k_3 (1 - \alpha^2) \}] \\
 &\quad \div 2 (1 - \alpha^2 - \beta^2 - \gamma^2 - 2\alpha\beta\gamma) (\omega_2^2 - \omega_3^2) (\omega_2^2 - \omega_1^2), \\
 s &= [\{ k_1 m^2 n^2 + k_2 n^2 l^2 + k_3 l^2 m^2 \} - \omega_3^2 \{ l^2 (k_2 + k_3) + m^2 (k_3 + k_1) \\
 &\quad + n^2 (k_1 + k_2) + k_1 k_2 k_3 \} + \omega_3^4 \{ k_1 (1 - \beta^2) + k_2 (1 - \gamma^2) \\
 &\quad + k_3 (1 - \alpha^2) \}] \\
 &\quad \div 2 (1 - \alpha^2 - \beta^2 - \gamma^2 - 2\alpha\beta\gamma) (\omega_3^2 - \omega_1^2) (\omega_3^2 - \omega_2^2).
 \end{aligned}$$

On inspecting these equations for damping coefficients it is noticed, at once, they are also correct with respect to the dimensions.

XXXIV. *On the Electrodynamic Potentials of Moving Charges.* By S. C. KAR, M.A., Professor of Mathematics, Bangabasi College, Calcutta*.

THE electrodynamic potentials of a moving charge or the electron have been the subject of several investigations and the earliest were those of Liénard† and Wiechert‡. Among recent writers who have found the potentials on a relativity basis may be named Sommerfeld§ and M. N. Saha||. Both of these writers performed a four-dimensional integration in the Minkowski space-time manifold and have obtained results which are quite general. It appears to the present writer that the Liénard and Wiechert result—and the method admits of easy extension to the case of a straight linear current—may be obtained easily enough by a Lorentz transformation to a rest-system and back without resort being had to four-dimensional integration.

* Communicated by the Author.

† *L'Éclairage électrique*, vol. xvi. pp 5, 53, 106 (1898).

‡ *Arch. Néerl.* vol. v. p. 549 (1900).

§ *Ann. d. Phys.* vols. lii. and liii.

|| *Phil. Mag.* vol. xxxvii. p. 347 (1919).

The equations for the potentials may be written

$$\square (ic\Phi, F, G, H) = \rho_0 \kappa (ic, u, v, w)$$

where

$$\kappa = 1 / \sqrt{1 - \frac{u^2 + v^2 + w^2}{c^2}}$$

and

$$\square = -\frac{\partial^2}{c^2 \partial t^2} + \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

It is well to point out that this mode of writing the equations is slightly different from the customary mode where $\square F' = \rho_0 \kappa''$ so that our F is cF' . This deviation from usage is justified by the greater symmetry and homogeneity of form resulting. The equations for h (magnetic intensity) and d (electric intensity) will on account of this change assume the forms

$$h = \frac{1}{c} \text{rot} (F, G, H),$$

$$d = -\frac{1}{c^2} (\dot{F}, \dot{G}, \dot{H}) + \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \Phi.$$

(2)

It is evident that the operator \square is an invariant under a Lorentz transformation. It will therefore follow that $(ic\Phi, F, G, H)$ is a four-vector, because $\kappa(ic, u, v, w)$ is a four-vector. Therefore $c^2\Phi\delta t - F\delta x - G\delta y - H\delta z$ which represents the scalar product of the four-vectors $(ic\Phi, F, G, H)$ and $(ic\delta t, \delta x, \delta y, \delta z)$ is invariant under a Lorentz transformation. Therefore,

$$c^2\Phi\delta t - F\delta x - G\delta y - H\delta z = c^2\Phi'\delta t' - F'\delta x' - G'\delta y' - H'\delta z',$$

where the dashes refer to a system of axes moving with velocity v along the axis of x .

$$\text{But } \delta x = \kappa(\delta x' + v\delta t'),$$

$$\delta y = \delta y', \quad \delta z = \delta z',$$

$$\text{and } \delta t = \kappa\left(\delta t' + \frac{v\delta x'}{c^2}\right), \quad \text{where } \kappa = 1 / \sqrt{1 - \frac{v^2}{c^2}}.$$

Substituting and equating coefficients of $\delta x'$, $\delta y'$, $\delta z'$, and $\delta t'$ we have

$$F' = \kappa(F - v\Phi), \quad G' = G, \quad H' = H,$$

and

$$\Phi' = \kappa\left(\Phi - \frac{vF}{c^2}\right).$$

These formulæ are exactly similar to the usual formulæ for δx , δy , δz , δt and connect the potentials for any system of axes with those of another moving with velocity v along the axis of x .

The reversing formulæ are

$$\begin{aligned} F &= \kappa(F' + v\Phi'), \quad G = G', \quad H = H', \\ \text{and} \quad \Phi &= \kappa\left(\Phi' + \frac{vF'}{c^2}\right). \end{aligned} \quad (3)$$

Let us suppose an electron moving with velocity v along the axis of x and let us take a system of axes moving with the electron. It is apparent that for the latter system of axes the electron is at rest. The vector potentials $(F', G', H') = 0$ and $\Phi' = \frac{e}{4\pi r'}$, due to a static charge e where r' is the distance of the point P at which the potentials are considered.

For the original system of axes, therefore, we should have according to the formulæ of transformation given above,

$$F = \kappa v \frac{e}{4\pi r'}, \quad G = 0, \quad H = 0, \quad \text{and} \quad \Phi = \kappa e \frac{1}{4\pi r'}.$$

r' is, however, expressed in terms of the coordinates of the rest system and it will be necessary to transform it to a form involving the coordinates of the original system.

But if the time-difference between the point P and the electron is $\Delta t'$, then

$$\begin{aligned} r' &= c\Delta t' \\ &= \kappa c \left[\Delta t - \frac{v\Delta x}{c^2} \right] \\ &= \kappa \left[r - \frac{v\Delta x}{c} \right] = \kappa r \left[1 - \frac{v}{c} \cdot \frac{\Delta x}{r} \right] \\ &= \kappa r \left[1 - \frac{v_r}{c} \right]. \end{aligned}$$

$$\therefore \quad F = \frac{ev}{4\pi r \left[1 - \frac{v_r}{c} \right]}, \quad G = 0, \quad H = 0,$$

$$\text{and} \quad \Phi = \frac{e}{4\pi r \left[1 - \frac{v_r}{c} \right]},$$

which are Liénard's results.

(4)

Let us suppose a straight linear uniform current to arise from continuous and uniform rush of electrons in the conducting wire in the direction of the current. Viewed from a system of axes moving with the common velocity of the electrons the phenomena reduce, as far as the rushing electrons are concerned, to the case of a linear and uniform distribution of electric charge. If N electrons each with charge $-e$ be supposed to rush with velocity v to the observer in the rest-system the linear density of static charge is $-Ne$.

From the ordinary theory of potential, the potential Φ' for such a distribution is $-2Ne \log r'$ where $r'^2 = y'^2 + z'^2$ and $(F', G', H') = 0$. Transforming to a moving system according to our formulæ we should have

$$F = \kappa v \Phi' = -2\kappa Nev \log r, \quad G = G' = 0, \quad H = H' = 0,$$

$$\Phi = \kappa \Phi' = -2\kappa Ne \log r \quad [\because r = r'].$$

The magnetic field therefore would be given by $h_x = 0$, $h_y = -\frac{2\kappa Nevz}{cr^2}$, $h_z = +\frac{2\kappa Ne y}{cr^2}$ and the electric field would be given by $d_x = 0$, $d_y = -\frac{2\kappa Ne y}{r^2}$, $d_z = -\frac{2\kappa Ne z}{r^2}$. In the conducting wire, however, there is also a linear distribution of positive nuclei at rest of which the potential would be $+2Ne \log r$.

The electric field due to these would be given by $d_x' = 0$, $d_y' = +\frac{2Ne y}{r^2}$, $d_z' = +\frac{2Ne z}{r^2}$.

The resultant electric field would therefore have the components 0 , $\frac{2Ne y}{r^2}(1-\kappa)$, $\frac{2Ne z}{r^2}(1-\kappa)$, and is of the order of $\frac{v^2}{c^2}$. The magnetic field is of finite magnitude and circular round the wire, the resultant being $\frac{2\kappa Nev}{cr}$ which is quite in accord with the expression $\frac{2(\text{current})}{r}$ if we put $\text{current} = \frac{\kappa Nev}{c}$ or $\frac{Nev}{c}$ neglecting quantities of the order $\frac{v^2}{c^2}$ in comparison with unity.

XXXV. *The Identical Relations in Einstein's Theory.*
By A. E. HARWARD*.

THE March number of the Philosophical Magazine contains an interesting proof of the identity

$$G_{\mu\nu}^{\prime} = \frac{1}{2} \frac{\partial G}{\partial x_{\mu}}$$

by Dr. G. B. Jeffery.

Apparently it is not generally known that this identity is a special case of a more general theorem which can be very easily proved. I discovered the general theorem for myself, but I can hardly believe that it has not been discovered before.

The theorem is

$$(B_{\mu\nu\sigma}^{\rho})_{\tau} + (B_{\mu\sigma\tau}^{\rho})_{\nu} + (B_{\mu\tau\nu}^{\rho})_{\sigma} = 0. \quad (1)$$

This identity can be verified in a rather laborious manner by forming the covariant derivative of $B_{\mu\nu\sigma}^{\rho}$, but it can be more easily proved as follows:—

The identity

$$A_{\mu, \nu\sigma} - A_{\mu, \sigma\nu} = B_{\mu\nu\sigma}^{\rho} A_{\rho} \quad (2)$$

can be easily generalized so as to apply to the case where instead of the vector A_{μ} we have a tensor of any order; thus

$$A_{\mu\nu, \sigma\tau} - A_{\mu\nu, \tau\sigma} = B_{\mu\sigma\tau}^{\rho} A_{\rho\nu} + B_{\nu\sigma\tau}^{\rho} A_{\mu\rho}.$$

This is proved in the same way as (2).

Now, if A_{μ} be any covariant vector, then

$$\begin{aligned} & (A_{\mu, \nu\sigma\tau} - A_{\mu, \nu\tau\sigma}) + (A_{\mu, \sigma\tau\nu} - A_{\mu, \sigma\nu\tau}) + (A_{\mu, \tau\nu\sigma} - A_{\mu, \tau\sigma\nu}) \\ &= (A_{\mu, \nu\sigma} - A_{\mu, \sigma\nu})_{\tau} + (A_{\mu, \sigma\tau} - A_{\mu, \tau\sigma})_{\nu} + (A_{\mu, \tau\nu} - A_{\mu, \nu\tau})_{\sigma}; \\ \therefore & B_{\mu\sigma\tau}^{\rho} A_{\rho, \nu} + B_{\nu\sigma\tau}^{\rho} A_{\mu, \rho} + B_{\mu\tau\nu}^{\rho} A_{\rho, \sigma} + B_{\sigma\tau\nu}^{\rho} A_{\mu, \rho} \\ &+ B_{\mu\nu\sigma}^{\rho} A_{\rho, \tau} + B_{\tau\nu\sigma}^{\rho} A_{\mu, \rho} \\ &= (B_{\mu\nu\sigma}^{\rho} A_{\rho})_{\tau} + (B_{\mu\sigma\tau}^{\rho} A_{\rho})_{\nu} + (B_{\mu\tau\nu}^{\rho} A_{\rho})_{\sigma}. \end{aligned}$$

* Communicated by the Author.

Now,

$$(B_{\mu\nu\sigma}{}^\rho A_\rho)_\tau = (B_{\mu\nu\sigma}{}^\rho)_\tau A_\rho + B_{\mu\nu\sigma}{}^\rho A_{\rho,\tau};$$

so after cancellation we get

$$\begin{aligned} (B_{\nu\sigma\tau}{}^\rho + B_{\sigma\tau\nu}{}^\rho + B_{\tau\nu\sigma}{}^\rho) A_{\mu\rho} \\ = [(B_{\mu\nu\sigma}{}^\rho)_\tau + (B_{\mu\sigma\tau}{}^\rho)_\nu + (B_{\mu\tau\nu}{}^\rho)_\sigma] A_\rho. \end{aligned}$$

The expression in brackets on the left vanishes identically. Since A_ρ is arbitrary, the expression in brackets on the right must also vanish. Q.E.D.

The identity

$$B_{\nu\sigma\tau}{}^\rho + B_{\sigma\tau\nu}{}^\rho + B_{\tau\nu\sigma}{}^\rho = 0$$

follows at once from the well-known identical relations between the Riemann symbols. The three-term identity is usually stated in the form

$$(\mu\tau\sigma\nu) + (\mu\sigma\nu\tau) + (\mu\nu\tau\sigma) = 0,$$

or in the modern notation

$$B_{\mu\nu\sigma\tau} + B_{\mu\tau\nu\sigma} + B_{\mu\sigma\tau\nu} = 0;$$

here $B_{\mu\nu\sigma\tau}$ denotes $g_{\tau\epsilon} B_{\mu\nu\sigma}{}^\epsilon = (\mu\tau\sigma\nu)$. Since $B_{\mu\tau\nu\sigma} = B_{\nu\sigma\mu\tau}$ and $B_{\mu\sigma\tau\nu} = B_{\sigma\mu\nu\tau}$,

$$\begin{aligned} 0 &= B_{\mu\nu\sigma\tau} + B_{\nu\sigma\mu\tau} + B_{\sigma\mu\nu\tau} \\ &= g_{\tau\epsilon} (B_{\mu\nu\sigma}{}^\epsilon + B_{\nu\sigma\mu}{}^\epsilon + B_{\sigma\mu\nu}{}^\epsilon). \end{aligned}$$

We assume that the determinant $g_{\mu\nu} = g$ does not vanish in the region under consideration; therefore the expression in brackets must vanish.

This identity can also be proved by observing that the expression

$$(A_{\nu,\sigma\tau} - A_{\nu,\tau\sigma}) + (A_{\sigma,\tau\nu} - A_{\sigma,\nu\tau}) + (A_{\tau,\nu\sigma} - A_{\tau,\sigma\nu})$$

vanishes if A_ν is the derivative of a scalar; for in that case

$$A_{\nu,\sigma\tau} = A_{\sigma,\nu\tau}, \quad A_{\sigma,\tau\nu} = A_{\tau,\sigma\nu}, \quad \text{and} \quad A_{\tau,\nu\sigma} = A_{\nu,\tau\sigma}.$$

If we contract (1) by putting $\tau = \rho$, we get

$$(B_{\mu\nu\sigma}{}^\rho)_\rho + G_{\mu\sigma,\nu} - G_{\mu\nu,\sigma} = 0. \quad . \quad . \quad . \quad (3)$$

If we contract this again by multiplying by $g^{\mu\nu}$, we get the familiar identity

$$2G_{\sigma\nu}^{\nu} - \frac{\partial G}{\partial x_{\sigma}} = 0; \quad . \quad . \quad . \quad . \quad (4)$$

for since $(g^{\mu\nu})_{\rho} = 0$,

$$\begin{aligned} g^{\mu\nu} (B_{\mu\nu\sigma}^{\rho})_{\rho} &= (g^{\mu\nu} B_{\mu\nu\sigma}^{\rho})_{\rho} = (g^{\mu\nu} g^{\rho\tau} B_{\mu\nu\sigma\tau})_{\rho} \\ &= (g^{\rho\tau} g^{\mu\nu} B_{\tau\sigma\nu\mu})_{\rho} = (g^{\rho\tau} B_{\tau\sigma\nu}^{\nu})_{\rho} \\ &= (g^{\rho\tau} G_{\tau\sigma})_{\rho} = G_{\sigma\rho}^{\rho}; \end{aligned}$$

similarly

$$g^{\mu\nu} (G_{\mu\sigma})_{,\nu} = (g^{\mu\nu} G_{\mu\sigma})_{,\nu} = G_{\sigma\nu}^{\nu}$$

and

$$g^{\mu\nu} (G_{\mu\nu})_{,\sigma} = (g^{\mu\nu} G_{\mu\nu})_{,\sigma} = (G)_{,\sigma} = \frac{\partial G}{\partial x_{\sigma}}$$

since G is a scalar.

Jersey,
13th May, 1922.

XXXVI. *Energy Partition in the Double Pendulum.*

By H. S. ROWELL*.

IN a letter to 'Nature' (July 28, 1921) the present writer gave a theorem on the double pendulum which is capable of interesting extension.

If the masses of the bobs are m and M and the respective amplitudes are a and A with suffixes to denote the normal modes, then the theorem states that

$$\frac{a_1 a_2}{A_1 A_2} = -\frac{M}{m}.$$

If this equation is squared and both sides multiplied by m^2/M^2 , we have

$$\frac{m a_1^2 n_1^2 m a_2^2 n_2^2}{M A_1^2 n_1^2 M A_2^2 n_2^2} = 1,$$

where n_1 and n_2 are the radian frequencies of the two modes. This equation may be readily interpreted thus:—

"The ratio of the kinetic energy of one bob to that of the

* Communicated by the Author.

other bob in one mode is the reciprocal of the corresponding ratio in the other mode."

Proceeding to the general case of an elastic system with two degrees of freedom, using Professor Lamb's notation,

$$2T = A\dot{\theta}^2 + 2H\dot{\theta}\dot{\phi} + B\dot{\phi}^2,$$

$$2V = 2V_0 + a\theta^2 + 2h\theta\phi + b\phi^2;$$

so that with a time factor = in

$$n^2(A\theta + H\phi) = a\theta + h\phi,$$

$$n^2(H\theta + B\phi) = h\theta + b\phi;$$

whence the product of the roots in θ/ϕ is $-\frac{bH-hB}{aH-hA}$.

If $H=0$ so that T is a function of squares of velocities, the product of the amplitude ratios is $-B/A$, or, in the double pendulum, $-M/m$.

If $h=0$ so that the potential energy is a function of squares of displacements, the product of the amplitude ratios is b/a , i. e. the ratio of the two stability coefficients. Thus in either case we have an energy relation. For the kinetic energy take

$$H=0 \quad \text{and} \quad \frac{\theta_1\theta_2}{\phi_1\phi_2} = -\frac{B}{A};$$

square and multiply by A^2/B^2 , and insert the frequencies.

For the potential energy take

$$h=0 \quad \text{and} \quad \frac{\theta_1\theta_2}{\phi_1\phi_2} = -\frac{b}{a},$$

which, when squared as before, yields a similar relation. The two results may be expressed in words thus:—

When the Kinetic or Potential Energy is written as a function of squares only, the ratio of the Kinetic or Potential Energy expressed in one co-ordinate to that expressed in the other co-ordinate for one normal mode is the reciprocal of the corresponding ratio for the other normal mode.

This investigation gives an insight in certain cases into the indeterminateness of the normal modes with equal periods.

XXXVII. *Velocity of Electrons in Gases.**To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

IN a paper in the *Jahrbuch der Radioaktivität und Electronik* (vol. xviii. p. 201, April 1922) H. F. Mayer gives an account of some of the formulæ obtained by different physicists for the velocity of ions or electrons in gases due to an electric force, and concludes that a formula recently given by Lenard is more correct than the others.

Among the other formulæ which are discussed, the author gives what purports to be an account of a formula for the velocity of an ion which I published in the 'Proceedings of the Royal Society' (A. vol. lxxxvi. p. 197, 1912), and states that this formula is so incorrect that it does not even give the right order of the velocity. I should like to draw attention to the way in which Mayer has misinterpreted the matter, and to quote the formulæ as I gave them for the different cases in which the mass of the ion is small or large compared with the mass of a molecule of the gas through which it moves.

On pages 199, 204, and 206 of my paper, three formulæ are given for the velocity U of an ion in the direction of the electric force X in terms of the mean free path l of the ion, its mass m , charge e , and velocity of agitation u which is supposed to be uniform and large compared with U .

The first of these is

$$U = Xel/mu, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and applies only to cases in which the mass of the ion is small compared with that of a molecule of the gas (an electron for example), since it is here assumed that after a collision with a molecule all directions of motion of the ion are equally probable.

I pointed out that when the mass of the ion is larger than that of a molecule of the gas, all directions of motion of the ion after a collision are not equally probable, and that in this case an ion travels a considerable distance (having an average value λ) after a collision in the direction in which it was moving before a collision. A more general formula for the velocity was given, which is

$$U = Xe(l + \lambda)/mu. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the mass m of the ion is so large compared with the

mass m' of a molecule of the gas that all directions of motion of a molecule become equally probable after a collision with an ion, it was shown that formula (2) reduces to

$$U = Xel/m'u, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

as in this case it may be seen that

$$\frac{l + \lambda}{l} = \frac{m}{m'}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

It will be observed that formula (2) reduces to (1) when λ is zero, that is when m is small compared with m' , so that either of these two formulæ may be applied to the case of an electron moving in a gas. Mayer, however, selects formula (3) to find the velocity of ions of small mass or electrons, although it is definitely stated in my paper that formula (3) refers to large ions, and the relation (4) on which it depends can only hold when m is greater than m' . As the correct formula (1) for electrons differs by the factor m'/m from formula (3), it is unreasonable to expect the latter formula to give the velocity of an electron.

The above formulæ, obtained by simple considerations when the velocities of agitation of all the ions are taken as being the same, are of course not absolutely exact. There is a numerical factor by which the expressions should be multiplied in order to allow for the variations of the velocity of agitation about the mean velocity. In the most interesting case, which is that of electrons moving in a uniform electric field, the value of the numerical factor is about .9, but it has not been determined exactly. The determination of this factor is very difficult, as the distribution of the velocities of agitation of the electrons depends on the energy of an electron which is lost in a collision, and experiments show that the proportion of the total energy of an electron which is thus lost depends on the velocity. This problem has been fully considered by F. B. Pidduck (*Proceedings of the London Mathematical Society*, ser. 2, vol. xv. pt. 2, 1915), who shows that under certain conditions the proportion of the velocities which differ largely from the mean velocity of agitation is much less than the proportion indicated by Maxwell's formula for the distribution.

It appears that the error introduced by taking the velocities of agitation as being all equal to the mean velocity may be no greater than when the velocity distribution is taken as being the same as that given by Maxwell's formula.

In order to obtain an exact formula for the velocity U it
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would be necessary to take into consideration the variation of the mean free path of an electron with its velocity of agitation, and the large reduction of the energy of an electron when ionization by collision takes place.

These points in connexion with the motion of electrons in gases have not been taken into consideration by Lenard, and it does not appear that his formula is more correct than others which have been proposed.

Yours faithfully,

JOHN S. TOWNSEND.

3rd May, 1922.

XXXVIII. *On the Electrification at the Boundary between a Liquid and a Gas.* By Professor H. A. McTAGGART, M.A., *University of Toronto* *.

MANY years ago, in the course of some experiments on the effect of an electric current on the motion of small particles in a liquid, Quincke (*Ann. d. Phys.* cxiii. p. 513, 1861) observed that small gas-bubbles in water moved as though negatively charged. Although a good deal of attention has been paid to the movement of solid and of liquid particles in such cases, very little effort has been devoted to the study of small spheres of gas suspended in a liquid—one obvious reason being the difficulty of controlling them while under observation. A systematic examination of their electrical properties ought, however, to yield further information as to the physics—and chemistry too—of surface layers.

Before the war experiments in this field were begun by the author in the Cavendish Laboratory under Sir J. J. Thomson, and some results were obtained. Measurements were made (*Phil. Mag.* Feb. 1914, p. 297) of the velocity, under a fall of potential, of small spheres of air in distilled water and their electrical charges were estimated. The effects on the charge of the addition of minute amounts of various inorganic electrolytes were studied. Results were obtained (*Phil. Mag.* Sept. 1914, p. 367) showing how the charge varies with the presence in the water of certain alcohols and organic acids, and a parallel was shown to exist between the variation of the electric charge and the surface tension.

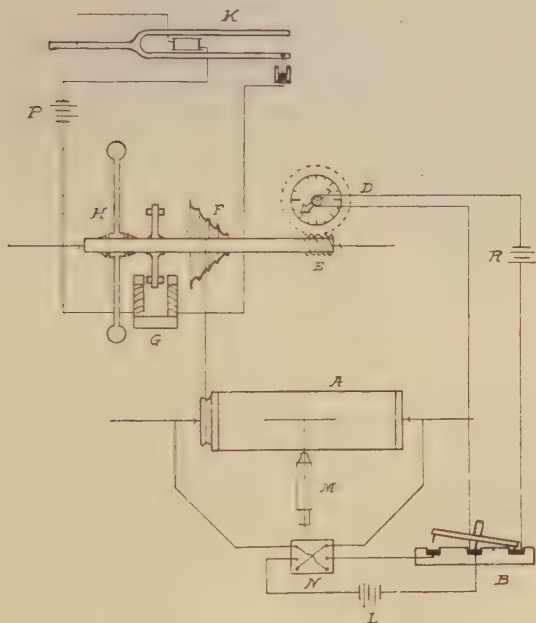
The present paper deals with some further experiments carried out in the University of Toronto, and describes the variation observed in the electric charge on small spheres

* Communicated by Professor J. C. McLennan, F.R.S.

of air when a particular electrolyte, Thorium Nitrate $[\text{Th}(\text{NO}_3)_4]$, was dissolved in water. This salt was selected for special study because it had been found to be unusually active in charging these surface layers.

The apparatus used was similar to that referred to in a former paper, one or two changes being made in it for greater convenience. The arrangement is shown in fig. 1.

Fig. 1.



A is a small cylindrical glass cell rotating about its axis on pivots and driven by a belt of thread from a pulley F on a Rayleigh motor. This motor was made in the laboratory workshop, and has, instead of the usual fly-wheel with a hollow rim filled with water, a solid brass wheel H—a modification suggested by Professor Wilberforce of Liverpool. The wheel, although loose on the shaft, has enough friction, when a heavy oil is used for lubricant, to keep the shaft in steady motion after synchronism with the tuning-fork is attained.

D is a timing device consisting of a vertical post carrying a pointer and made to rotate by a toothed wheel working in

the worm E. The pointer rests by its own weight on the top of the post, but at any instant in its motion over the fixed dial D it may be raised and stopped by a small electromagnet controlled by the key B. When released it falls back on the post and begins to record time with the same regularity as the tuning-fork. It forms a very convenient stop-watch if velocities are to be measured.

A travelling microscope M measures the distance travelled by any bubble on the axis of the rotating cell.

The water used was twice distilled—the second time in “Pyrex” glass and condensed in a silver coil.

The thorium nitrate was by Merck, and was assumed to have 12 H₂O—water of crystallization.

A stock solution was made up containing 4×10^{-6} equivalents per c.c. (1/250 normal), and from this other solutions were made by successive dilution.

A first series of readings was taken with various concentrations of the salt, but with bubbles of nearly the same size in order to reproduce the effects previously observed—the method of working being to fill the cell A with the desired solution, introduce a single bubble of air with the gas pipette, and set the cell in rotation. The bubble very soon takes up a steady position on the axis, and its motion under any fall of potential L may be examined.

Very small concentrations sufficed to reduce to zero the natural negative charge found in pure water and to give the small sphere of air a positive charge.

The following readings are typical :—

Fall of potential 34 volts per cm.
Diameter of bubble..... 0.3 mm.

Concentration, Equivalents per c.c.	Sign of charge.	Velocity of bubble. cms./sec./volt./cm.
4×10^{-7}	+	5×10^{-4}
4×10^{-8}	+	slower
8×10^{-9}	+	very slow (1.5×10^{-4})
5.7×10^{-9}	—	slow
4.7×10^{-9}	—	faster
4×10^{-9}	—	faster
Pure water	—	4×10^{-4}

The zero point was reached at a concentration of about 7×10^{-9} , a result rather higher than that given in a former paper. The salt was an entirely different sample, and may not have contained the same proportion of water of crystallization. (See Abegg and Auerbach, 'Inorganic Chemistry'.)

A series of readings was then taken for spheres of air of different sizes, one object being to observe the charge on very small spheres. It is very difficult, by the use of any kind of pipette, to introduce into the rotating cell bubbles smaller than 1.5 mm. in diameter. To avoid this difficulty the following mode of working was adopted. The solution was first placed in a partial vacuum to remove as much dissolved air as possible, and afterwards poured into the cell. A bubble into this gas-free solution slowly decreased in size by absorption until it vanished, while the electric charge could be observed at any stage.

Under these circumstances it was found that for a suitable concentration of solution a sphere of air which began with a small negative charge almost invariably and in a regular way reduced its charge to zero, and gradually took on a positive charge.

The following readings illustrate this point —

No. 1.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9} \times 5.7$	0.26	—
	0.17	—
	0.14	—
	0.10	0
	0.08	+

No. 2.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9} \times 5.7$	0.44	—
	0.35	—
	0.26	—
	0.17	0
	0.14	+

No. 3.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9} \times 5.7$	0.62	—
	0.53	—
	0.39	+
	0.17	+
	0.08	+

No. 4.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9} \times 5.7$	0.71	—
	0.53	—
	0.44	—
	0.35	0
	0.32	+
	0.23	+

No. 5.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9} \times 5.7$	0.28	—
	0.17	—
	0.08	—
	0.05	—

It will be seen from the first four examples given that at a concentration of $10^{-9} \times 5.7$ the change of sign occurs in every case. Rarely, as in No. 5, and then only when the original sphere was small, did the sign remain the same. Even then the charge grew steadily less. In practically every case the negative charge slowly decreases as the bubble gets smaller, passes through zero, and increases to a small positive value.

Three examples are given for slightly greater concentrations:—

No. 6.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9} \times 6.6$	0.53	—
	0.41	0
	0.35	+
	0.17	+
	0.08	+

No. 7.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9} \times 6.6$	0.35	—
	0.28	0
	0.26	+
	0.17	+
	0.14	+

No. 8.

Concentration. Equivalents per c.c.	Diameter of sphere in mm.	Sign of charge.
$10^{-9} \times 8$	0.44	Almost zero.
	0.35	+
	0.17	+

Above a concentration of $10^{-9} \times 8$ the bubbles were always positive.

The examples given show that the spheres do not all have the same size when they reach the zero—isoelectric—point in a given solution. The larger a sphere is at the beginning the larger it is when its charge becomes zero. This suggests, as the cause of the change in sign, a kind of coagulation of something in the free surface.

It is known that, in a solution of thorium nitrate in water,

hydrolysis occurs with the formation of thorium hydroxide thus—



There is present in the solution some of the original salt, some acid, and the hydroxide in colloidal form. The presence of the last-mentioned was suspected as one of the causes producing the reversal of sign, and experiments were then made to test its activity in altering the charge.

A colloidal solution of thorium hydroxide as free as possible from salt and acid was prepared by dialysis (Burton, 'Physical Properties of Colloidal Solutions,' 2nd Ed., p. 16). A dialysing "sleeve" shaped in the form of a test-tube was made of "parlodion" (sold by the Du Pont Chemical Co., New York). A solution of the parlodion in ether and alcohol was used to coat the inside of a test-tube of suitable size. After the solvent had evaporated the parlodion remained as a thin but strong film which when detached from the glass served very well as a dialysing vessel.

For this experiment a solution containing about 2 gm. of salt in 50 c.c. of water was dialysed for a period of three weeks, after which an estimate was made of the colloid present. A sample of 10 c.c. evaporated over sulphuric acid gave a residue of .0034 gm. The residue formed a thin layer of gelatinous material on the bottom of the evaporating dish, with drying cracks across it in all directions.

The effect of this colloid on the charge on small spheres of air in water was then examined, the dialysed solution above mentioned being diluted as shown in the following examples :—

No.	C.c. colloid solution in 100 c.c. water.	Diameter of sphere in mm.	Sign of charge.
1	10	0.21	+
		0.12	+
		0.07	+
2	5	0.17	+
3	2.5	0.17	+
		0.07	+

It is seen that the surface is charged positively by the presence of very small amounts of the colloid.

The following examples show the gradual reversal of the

sign of the charge accompanying the absorption of the bubble :—

No.	C.c. colloidal solution in 100 c.c. water.	Diameter of sphere in mm.	Sign of charge.
4	1.0	0.17	—
		0.14	+
5	0.5	0.35	—
		0.26	—
		0.12	+
		0.05	+
6	0.25	0.32	—
		0.17	—
		0.08	—
		0.05	+

The experiments show that the colloidal thorium hydroxide gives both the effects observed with the ordinary solution. It not only charges the surface positively if present in sufficient amount, but it also exhibits the reversal of charge with diminishing size of the bubble, and this, too, in concentrations of thorium of about the same order as in the case of the salt.

Discussion.

The state of the matter and the nature of the electric forces in surface layers of liquids is still a subject on which no very clear ideas exist. Experiments on electro-endosmosis all point to a selective action in such layers so far as the ions in the solution are concerned. But the observations are always complicated by the presence in contact with the liquid surface of a solid whose role in the selecting we are ignorant of. The same is true of cataphoresis experiments with solids, as, for example, in the study of the electrical charge on colloidal particles. This difficulty is avoided, however, in similar experiments with small spheres of air—or any gas—and in such cases we can safely regard any effects observed as due largely to the properties of the liquid and its free surface. In particular, the electrical charge existing at any air-liquid surface may be considered as the result of forces residing altogether in the liquid. It ought to be possible, then, in considering potential differences at solid-liquid junctions to isolate the contribution of the liquid.

In the case of thorium nitrate in solution the selective

action of the air-water surface is very marked, a positive charge being acquired by the surface with very minute concentrations of the salt. The positive ions available for selection are Th^+ and H^+ , but neither of these separately can be responsible for the unusual activity of the salt. The mere presence of H^+ ions, as, for example, in the form of an acid, does not produce so great an influence on the surface charge. Nor can free Th^+ ions have much effect, for they disappear in the dialysis and yet leave the pure colloidal solution practically as active as before. The real agent must be the particles of colloidal thorium hydroxide which gather about them groups of H^+ ions and carry them into the surface in larger numbers than would be possible for the H^+ ions alone.

The nature of this selective action must be connected with the shape of the surface, or, to put it in another way, a particle must reach a certain size before it can be regarded as having a surface-layer about it with a tension and an electric charge. We have at present in order of size—ions, ionic micelles (Prof. McBain, "Soap Solutions," *Nature*, March 10, 1921), ultra-microscopic colloidal particles, microscopic and macroscopic particles including gas-bubbles. At what stage a surface-layer is formed it is difficult to say, but it seems reasonable to suppose that the curvature of such a surface would have an effect on the charge adsorbed. The change of sign with decreasing size of air-sphere shown in these experiments seems to bear out this idea.

The information obtained regarding the effect of thorium nitrate on the electrification of air-water surface layers may be summarized as follows:—

1. Thorium nitrate in aqueous solution and in concentrations as small as 8×10^{-6} normal gives a positive electric charge to the surface of a sphere of air immersed in it. (In distilled water the charge is always negative.)

2. For concentrations in the neighbourhood of 6×10^{-6} normal a sphere initially negative becomes gradually positive as the sphere diminishes in size.

3. Colloidal thorium hydroxide in small concentrations of the same order also gives a positive electric charge to a sphere of air immersed in it.

4. Colloidal thorium hydroxide also exhibits the reversal of the sign of the charge with a decrease in the size of the bubble.

5. It is suggested that this reversal of sign is experimental evidence of a relation between the curvature of the surface and its adsorptive power.

FIG. 1.



FIG. 2.

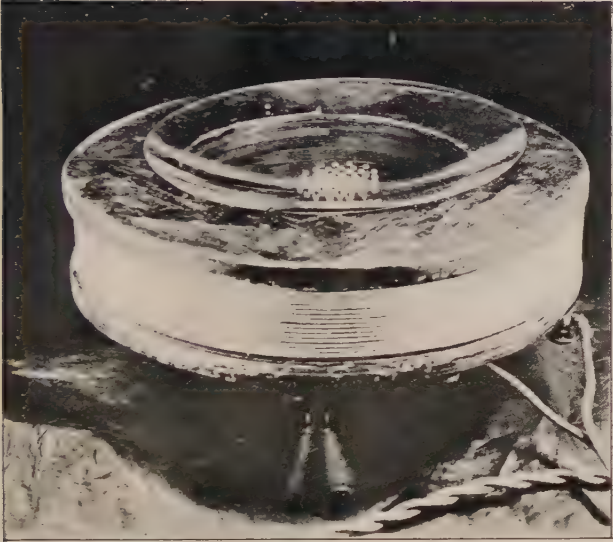


FIG. 6.



FIG. 3 (a).

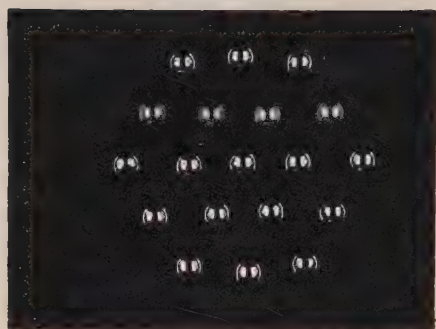


FIG. 3 (b).



FIG. 4.

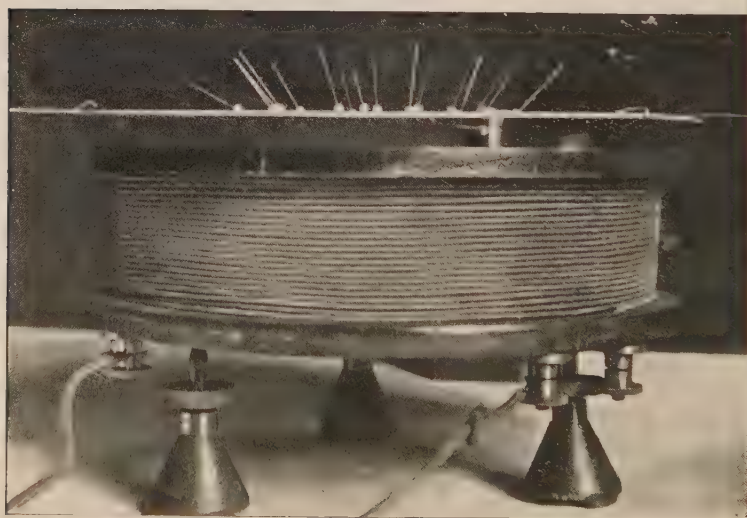


FIG. 5 (a).

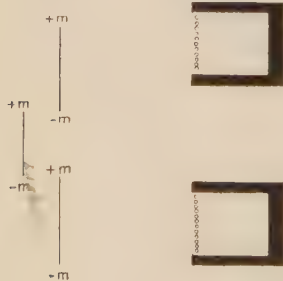


FIG. 5.

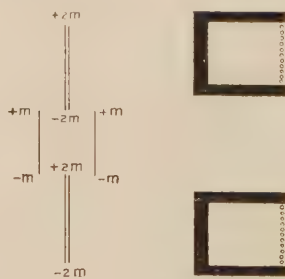
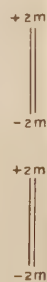


FIG. 5



The experiments are being continued as time permits in the hope of obtaining some new information regarding these free surfaces. It is the intention to compare with thorium the effects of one or two other tetravalent and trivalent metals in the colloidal state.

I wish to thank Professor J. C. McLennan for his kind and encouraging interest in the work.

XXXIX. *Note on a Lecture-Room Demonstration of Atomic Models.* By LOUIS V. KING, D.Sc., Macdonald Professor of Physics, McGill University*.

[Plate II.]

Section 1.

SEVERAL mechanical models illustrating various types of atomic structure have been proposed from time to time. Among these we may mention Mayer's classical experiments with floating and suspended magnets, illustrating the action of atomic forces †.

Many modifications of these classical experiments have been suggested. In particular, a paper by R. Ramsey describes interesting modifications of the original apparatus ‡.

Actual apparatus illustrating the supposed structure of atoms can now be obtained ready for use from scientific instrument makers §.

All these methods involve the repulsive forces between steel elements (needles or spheres) in a permanent magnetic field, together with the central attraction set up by a permanent magnet. An important point contributing to the success of the experiment is that all the magnets, representing electrons, have as nearly as possible equal pole strengths. Owing to magnetic reluctance and effects of demagnetization, these conditions are difficult to realize in practice without a considerable amount of care and expenditure of time.

* Communicated by the Author.

† J. J. Thomson, 'Corpuscular Theory of Matter' (1907), Chapter 6, pages 103 *et seq.*

‡ R. R. Ramsey, "The Kinetic Theory of the Electron Atom." Proceedings of the Indian Academy of Sciences, 1918. Phil. Mag. vol. xxviii. Feb. 1917, pp. 207-211.

§ W. M. Welch, Scientific Company, Chicago.

Section 2.

The magnetic elements which form the essential feature of the apparatus to be described consist of a number of steel spheres or small soft-iron rods magnetized in a strong alternating field.

One such model is shown diagrammatically in Pl. II. fig. 1, while fig. 2 shows the actual apparatus. The coil A consists of 340 turns of number 12 B. & S. copper wire (2 mm. diam.); inside radius of winding 8.8 cm., outside radius 13.5 cm., width of coil 3.9 cm. Such a coil has a resistance of approximately 1.3 ohms and self-inductance of about 32 millihenries. It may be connected directly to a 110-volt 60-cycle A.C. circuit without overheating. In such circumstances it draws a current of about 9 amperes. It is approximately of such dimensions as to give a maximum field strength at the centre of the coil.

Placed over the opening of the coil is a large watch-glass B whose radius of curvature is approximately 25 cm. If available, an accurately ground concave glass mirror may be used to advantage. If, now, a supply of steel ball-bearings about 3 mm. in diameter is available, these may be placed on the concave surface B, where they will experience an attraction towards the lowest point approximately proportional to the distance. When the maximum current is passed through the magnetizing coil, the steel spheres will become A.C. magnetic doublets of very uniform magnetic moments. It will be noticed that the magnetic axis will always be very accurately along the direction of the magnetic field, independently of the rolling motion of the balls. Furthermore, if the spheres are of fairly uniform quality and the field strength sufficiently great, the instantaneous magnetic moments of these doublets will be equal in magnitude and phase. In these circumstances the steel spheres will repel each other with a force varying as the inverse fourth power of the distance, the constant of proportionality being accurately the same for all the spheres. With the attraction to the centre varying as the distance, it may be expected that the magnetic elements will form remarkably symmetrical stable groupings. One such grouping is illustrated in Pl. II. fig. 3 (*a*).

It is obvious that by a very simple arrangement of lenses and mirrors this model atom may be projected on a screen. The concave surface B may, if desired, be mounted so as to allow of rotation, thus increasing the interest of the "atomic" arrangements. This experiment is extremely convenient for lecture-room purposes, as it requires no preparation and is

always certain to give results which never fail to delight an audience.

An interesting variant of this experiment is to make use of the arrangement of two coils described in Section 5 (figs. 5 & 6). A surface of clean mercury is placed midway between the two coils. A number of steel balls floating on this surface will repel each other as already described, and will all tend towards the centre, owing to the greater intensity of field. The remarkably regular arrangement taken up under these conditions is shown in fig. 3 (*b*). The damping is so slight that the system may be set into oscillation in various ways by means of external magnets, giving a good illustration of internal vibrations in the atom. It would, moreover, be possible with no very great expenditure of labour to determine the frequency of various modes and compare the results with theoretical calculations.

Section 3.

The same apparatus may also be used to illustrate the motion of the molecules of gas or the Brownian movements. For this purpose an elongated piece of iron is employed, *e. g.* a short cylinder of iron or steel wire about 1 cm. in length by 1 mm. in diameter. In the alternating field of the coil such a magnet experiences a very strong torque, which vanishes when the axis lies along the direction of the resultant A.C. field. If such a magnet is placed in a flat cylindrical glass vessel occupying the centre of the coil, and the field suddenly applied, violent movements of the little iron rod will be observed. The instantaneous moments set up by the field will be sufficient to make the rod leave the surface on which it is resting and describe a trajectory under the combined effect of gravity and the magnetic field. At the termination of the flight, it will again strike the glass plate and will then receive an additional impulse made up of the magnetic torque and the elastic reaction at contact with the glass. This will start it on a new trajectory, and the process will be continued indefinitely until the rod makes contact with the plate at the termination of its flight in such a way that the instantaneous torque is zero. Then it stops dead with the axis pointing along the direction of the field. This is an event which happens very rarely. Several such rods enclosed within a glass vessel will keep in constant motion in a manner resembling the motion of molecules in a rarefied gas. An interesting variant of this experiment is to insert short steel wires along the diameters of small pith balls which hop around, describing flights in the glass vessel as if

they were animated with life. As before, the glass vessel and its contents may be projected on a screen, the resulting effect being illustrative of molecular movements.

Section 4.—Experiments on Electrodynanic Repulsion.

Owing to the distribution of the magnetic field around the coil employed in this experiment, the same apparatus is well suited to the demonstration of electrodynanic repulsion. For this purpose several plates of aluminium or copper should be cut with a radius approximately equal to the outer radius of the coil. Such a disk may be anchored by three strings fastened at equidistant points of the circumference so as to allow it to move vertically, with its centre over the axis of the coil, which is laid in a horizontal position. On applying A.C. circuit, the plate will float three or four centimetres above the coil. By placing a light iron rod (3 cm. \times 1 mm.) on the plate, the direction of the A.C. field is easily demonstrated, as shown in Pl. II. fig. 4. It will be noticed that over an annular region bounded by the outer edge of the plate and a circle of half its radius, the lines of force are inclined at approximately 45° to the vertical. It is the reaction of the horizontal component of the A.C. field with the induced current due to the vertical component which causes the repulsion referred to. To demonstrate this, a circular plate may be cut up into several concentric rings and laid on a sheet of glass. When current is applied it is only the outer rings which are repelled, the force on the inner rings gradually becoming less, until that on the central disk in a practically uniform field perpendicular to its plane is practically *nil*.

Iron filings poured on a glass plate laid horizontally over the coil assume an interesting laminar distribution, which again may be projected on a screen. The iron filings tend to arrange themselves in a series of vertical planes about 1 cm. high arranged radially. It is easily seen that this arrangement is due to the fact that under the influence of the alternating field, each of the radial planes represents a series of vertical A.C. magnets which repel each other. Their height is limited by the vertical stability of the plates under the combined effect of gravity and of the alternating field.

Section 5.—Experimental Model of the Rutherford Atom.

By using two coils of the dimensions already described, arranged with their planes horizontal at a distance apart equal to the mean radius (Helmholtz arrangement), it is

possible to secure a fairly uniform field over a considerable area midway between the coils. Such arrangement (Pl. II. figs. 5 & 6) allows of interesting experiments on a model atom approximating more closely to modern ideas. A shallow circular basin of mercury is placed on an adjustable stand between the two coils. A number of steel pins with glass heads serve as the elements (electrons) for the model. If one of these is placed with the glass head on the mercury surface, it will float in a vertical position and tend to move towards the centre of the field, owing to the greater concentration of lines of force. This force towards the centre may be varied at will by adjusting the height of the mercury surface, or by placing rods of soft iron along the axis of the coils at adjustable distances above or below the mercury surface. If a second pin be floated on the mercury surface, it will repel the first with a force varying nearly as the inverse square law when the distance apart is not too great. A third pin may be added, when a triangular arrangement will be formed. Successive pins give the familiar series of regular polygons arranged in concentric rings. It is evident that the great advantage of the A.C. field is to make the magnetical polarity of each of the pins very nearly equal, thus giving rise to a remarkable symmetry in the arrangements formed, as illustrated by figs. 7 (*a*) and 7 (*b*) (Pl. II.). As before, the experiment can be carried out in such a way that the various stable arrangements may be projected on a screen. It is extremely simple to demonstrate the apparatus at a moment's notice, the only precaution necessary being to use clean mercury so as to allow a great mobility of the floating pins on an uncontaminated surface.

It is interesting to notice that rotation of the basin containing mercury does not disturb any particular stable arrangement, owing to the fact that the centrifugal force is accurately balanced by the change of slope of the paraboloidal mercury surface.

The use of an A.C. field allows of the possibility of realizing positive electrons and a central nucleus, the law of forces between them being very nearly that of the inverse square and at the same time very exactly that corresponding to charges of $\pm e$, $\pm 2e$, $\pm 3e$, etc. It is evident from fig. 5 (Pl. II.), illustrating the model under consideration, that electrons may be represented by lengths of soft-iron wire of the same diameter arranged to move with both ends in the same plane at distances not too far apart compared with their length. In these circumstances we have repulsion according to the inverse square law, the charge $-e$ being represented

by the average pole strength $\pm m$ of each rod, which is extremely uniform. A nucleus of positive charge ne may be made up by taking $2n$ lengths of the same wire and inserting them in a small glass or aluminium tube, as shown in fig. 5, illustrating a nucleus of charge $+2e$. In these circumstances, each of the rods representing electrons is *attracted* to the nucleus with a force varying nearly as the inverse square of the distance and proportional to $nm \times m$, the average pole strength of each end of the rod being $\pm m$.

In order to realize this arrangement, the rods (about 7 cm. \times 1 mm. diameter), representing negative electrons, should be suspended from silk fibres about 1 metre or more in length. By adjusting the position of the rods in the space between the coils, a position of neutral equilibrium may be found in which there is practically no tendency for the rods to move either towards the centre or radially outwards. Under the combined effect of gravity and of the magnetic field they seem to float in any position. When this adjustment has been made, the rods representing the nucleus should be set in position along the axis of the coils. The suspended rod representing the electron may then be projected so as to describe a path about the fixed nucleus, and a damped elliptic orbit will be observed, the nucleus being at one focus.

If two lengths of wire are used to make up a nucleus $+e$ in the manner illustrated by fig. 5 (a), we obtain a model of the hydrogen atom which is dynamically stable.

If we make up positive nucleus of charge $2e$, represented by two pairs of iron rods, we obtain a model (fig. 5 (b)) of the ionized helium atom which is dynamically stable. If we introduce an additional iron rod representing an electron (fig. 5), and therefore a complete helium atom, it seems impossible to obtain a dynamically stable arrangement by any circumstances of projection. For instance, any attempt to reproduce the symmetrical oscillation suggested by Langmuir meets with failure, owing to the dynamical instability of this arrangement.

It is obvious that further experiments along these lines, leading possibly to results of great interest, might be carried out by constructing large solenoidal coils to give a uniform A.C. field, in which circumstances the inverse square law of attraction and repulsion between electrons and nuclear charges ne ($n=1, 2, 3$, etc.) would be faithfully reproduced.

XL. The Influence of the Size of Colloid Particles upon the Adsorption of Electrolytes. By HUMPHREY D. MURRAY, Exhibitioner of Christ Church, Oxford.*

SEVERAL workers have examined the influence of concentration upon the coagulation of colloidal solutions, but references to the effect produced by alteration in the degree of dispersion are few and not very definite. Kruyt and Spek † examined the coagulation of colloidal arsenious sulphide, and found that the coagulative value of univalent ions increased with increasing dilution; in the case of a divalent ion there was a slight decrease; whilst for a trivalent ion there was a rapid decrease in the coagulative value. Burton and Bishop ‡ examined the coagulative values of various ions upon colloidal solutions of arsenious sulphide, copper, and gum mastic, and as the result of their experiments found that with univalent ions the concentration of the ion required for coagulation increased with decreasing concentration of the colloid, for divalent ions the concentration of the ion was nearly constant, for trivalent ions the concentration of the ion varied almost directly with that of the colloid. More recently Weiser and Nicholas § have extended these researches to colloidal solutions of hydrous chromic oxide, prussian blue, hydrous ferric oxide, and arsenious sulphide. They found in the case of the first three that the coagulative values of electrolytes tended to increase with dilution of the colloid, but the increase was less marked with electrolytes having univalent precipitating ions, and became more marked as the valency rose. Odén found that sols with ultramicroscopic particles are more sensitive to electrolytes than those containing amicros.

The object of these experiments was to examine the influence of the size and uniformity of colloid particles upon the adsorption of electrolytes as measured by the minimal concentration for coagulation. For this it was necessary to obtain solutions of the same colloid prepared under identical conditions, but containing particles of different mean size. It was decided to employ Odén's method of fractional coagulation. The most suitable colloid to use, therefore, is one which, when first made, contains particles of markedly

* Communicated by the Author.

† Kruyt and Spek, *Koll. Zeit.* xxv. p. 1 (1919).

‡ Burton and Bishop, *Jour. Phys. Chem.* xxiv. p. 703 (1920).

§ Weiser and Nicholas, *Jour. Phys. Chem.* xxv. 742 (1921).

different size, and is stable when precipitated, redispersed, and dialysed. Gum mastic was found best to meet the requirements, and was used in the subsequent experiments. To show that the solutions employed were comparatively stable, the concentration of NaCl required to precipitate one of the fractions at the beginning and end of the experiments was measured and found to be :—

Feb. 15th	433 millemols.
Mar. 29th	439 ,,

Fractionation.

One gram of finely-powdered picked gum mastic was dissolved in about 20 c.c. of alcohol, and poured slowly with vigorous stirring into one litre of distilled water. By this method seven litres of mastic solution were prepared. Odén recommends that in all cases NaCl should be used for the precipitation. With mastic this necessitates a very large concentration of salt, which appears to be strongly adsorbed, and comes slowly through the dialyser. It was thought better to employ HCl, which precipitates in smaller concentration. It was found convenient to separate the mastic into seven fractions with these concentrations of HCl :—

Fraction.	Concentration of HCl in millemols.	Condition of Precipitate.
I.....	0-1.1	trace
II.....	1.1-1.4	good
III.....	1.4-1.7	
IV.....	1.7-2.0	..
V.....	2.0-2.3	..
VI.....	2.3-2.6	small
VII.....	2.6-2.9	trace

The procedure was as follows :—200 c.c. of the mastic solution were mixed with a quantity of $\frac{N}{10}$ HCl to give the required concentration, and then poured into the centrifuge vessels and allowed to stand for 60 minutes from the moment of mixing. It was then centrifuged at 3000 r.p.m. for 30 minutes. At the end of this time the supernatant liquid was poured off and the precipitate carefully shaken up with about 100 c.c. of distilled water. Fractions II. and VI. were retained until about 1500 c.c. of each had accumulated; the other fractions were rejected. At the same time 1500 c.c.

of mastic were completely coagulated with a concentration of 3.0 millimols. of HCl, and redispersed in an equal quantity of water. It appears below as solution B. It is to be expected that Fr. II. will contain particles of an average size greater than those in Fr. VI. and both will contain particles of more uniform size than those in solution B.

The solutions after dispersion were kept in dialysers of parchment paper until the dialysate was uncontaminated with HCl. They were then placed in perfectly clean vessels of resistance glass fitted with a siphon, and a soda-lime tube attached to the air-inlet. The siphon pipes were closed by short pieces of rubber tubing and pinch cocks.

Basis of Comparison.

Any method of comparison between two or more solutions based upon the total masses of the disperse phase in unit volume is useless when applied to data due to adsorption. It is possible to take as a basis the number of particles in unit volume, or, what is probably more characteristic and capable of giving more directly comparable results, the total interfacial surface in unit volume. The former may in most cases be ascertained by a direct count under the ultramicroscope. To evaluate the latter it is necessary, beyond this, to know the total mass of the disperse phase, which can be effected by weighing after evaporation to dryness, or by the methods of volumetric analysis. In addition it demands a knowledge of the density of the disperse phase, or of the specific gravity of the solution and of the dispersion medium.

Perrin in his researches upon Brownian movement obtained the density of the mastic with which he was working by evaporating a portion of his suspension to dryness and estimating the density of the solid mastic. This value (1.064) he found to agree admirably with the density as determined from specific gravity measurements. It seems uncertain, however, as Burton* has pointed out, whether it is justifiable to assume that the density of the particles in the ordinary colloidal solution of gum mastic is the same as that of the solid substances. Perrin, as a matter of fact, used a suspension of mastic which had been obtained by centrifuging the larger particles from a solution of mastic and rejecting the remainder. In the case of the present solution, it seemed desirable to determine the density of the particles directly, with a pycnometer.

* Burton, 'Physical Properties of Colloidal Solutions,' 2nd Edition, p. 125.

Concentration of Mastic.

Thirty c.c. of the three solutions were evaporated slowly to dryness in a steam oven, and, as a mean of several determinations, gave the following weights of mastic in 10 c.c. of solution :—

	Weight found.
Solution B	·00463 gms.
Fr. VI.	·00171 „
Fr. II.	·00339 „

Number of Particles.

A true ultramicroscope was not used to count the particles, but a cardioid condenser, fitted to an ordinary microscope. The chief difficulty in work of this nature is to ascertain accurately the volume of the liquid within the field of view. A cell was made according to the recommendations of Siedentoff*, the only alteration made being the substitution of heavy glass for fused quartz. Fluorescence due to the glass was not sufficient to render difficult the counting of the comparatively large mastic particles. The cell consists of a glass plate, 5 cm. in diameter and 1·0 mm. in thickness, provided with a circular groove. The portion enclosed by the groove, 1 cm. in diameter, was polished exactly $2\ \mu$ deeper than the surface of the plate. This was used with a cover slip about ·25 mm. in thickness. The cell was soaked in concentrated sulphuric and chromic acids, washed with water, and then passed through two solutions of re-distilled alcohol. It was finally flamed. The source of illumination was a Pointolight lamp, fitted with a condenser. All the solutions examined were diluted with water which had been carefully distilled and allowed to stand for a month undisturbed. It contained on an average 1 particle in 20 counts in a volume of $14\cdot1 \times 10^{-5}$ cu. mm. and could, therefore, be considered optically pure to the degree of accuracy to which work was carried. All the solutions were contained in vessels of resistance glass, closed with corks covered with tinfoil. The method of procedure was to transfer, by means of a clean platinum loop, a very small drop of the solution to be examined to the central portion of the cell. The cover slip was laid on and pressed down until the Newton interference rings appeared at the edges. The dilutions were such that, when viewed with a convenient stop in the eyepiece, about three or four particles appeared

* Siedentoff, *Verhd. Deut. Phys. Ges.* xii. p. 6 (1910).

in the field of view. One hundred counts were taken at half-minute intervals, and the average number deduced from this. A few of the particles, especially in the case of Fr. II., tended to adhere to the walls of the cell, and to prevent any error due to this, the field of view was shifted five times during each count.

The results obtained were as follows :—

Solution.	Dilution.	Objective.	Eye-piece.	Diam. of Field of view.	Volume of Field of view.	Average No. of Particles.
Soln. B..	×726	4 mm. f.l.	×12	·30 mm.	$14\cdot1 \times 10^{-5}$ mm. ³	4·1
Fr. II..	×396	"	×12	·30 "	$14\cdot1 \times 10^{-5}$ "	3·0
Fr. VI..	×396	"	×18	·20 "	$6\cdot28 \times 10^{-5}$ "	4·0

Density of the Particles.

The density of the solutions was determined with an accurate pycnometer in a thermostat at 17·2° C. The weighings agreed to ·0002 gm. Fr. VI. was too dilute to give accurate results. The specific gravity of each solution rose slightly during dialysis, owing probably to the removal of adsorbed or dissolved alcohol. This rise continued for about five days. The weighings were made at the end of ten days. The dialysis was then continued in more efficient dialysers made by Soxhlet thimbles impregnated with collodion, but the specific gravity remained constant. As a mean of four weighings for each solution, the following values for the density of the particles were obtained :—

Soln. B. = 1·195.

Fr. II. = 1·186.

As a mean the density of the mastic was taken to be 1·190. This value is considerably higher than the density of the mastic in bulk, owing possibly to changes occurring either on dispersion, or coagulation. Perrin* states that he observed the density of his carefully washed granules apparently to rise in salt solutions, and this may account in part for the difference.

Size of Particles.

From these three sets of data—the number of particles in unit volume, the total mass of mastic in unit volume, and the density of the particles—it is possible to calculate the mean

* Perrin, *Ann. Chim. Phys.* xviii. p. 5 (1909).

radius r of the particles in each liquid. Of these three measurements that of the density seemed possibly least accurate, but, as it occurs in each calculation, the relative sizes remain unchanged.

Solution.	No. of Particles in mm. ³ ($=n$).	Total Mass of Particles in 10 c.c.	Mean volume of one particle.	Radius ($=r$).	$r^2 \times n \times 10^{-3}$.
Soln. B..	211×10^5	0.046 gm.	$1.83 \times 10^{-2} \mu^3$	$.164 \mu$	564
Fr. II..	84.2×10^5	0.034 „	$3.40 \times 10^{-2} \mu^3$	$.201 \mu$	340
Fr. VI..	252×10^5	0.017 „	$.57 \times 10^{-2} \mu^3$	$.111 \mu$	307

$r^2 \times n$ is a measure of the interfacial surface in unit volume.

Borjeson * has successfully combined the principle of gilding metal particles with observation of the rate of sedimentation of the particles so gilded, to measure the size of the original particles. He failed to obtain successful results with gelatine and gum arabic sols. An attempt to apply this method to the mastic solutions as a check on the results obtained also met with failure. It appears therefore unsuitable for organic colloids.

Rate of Coagulation.

It has been customary to fix an arbitrary time during which the colloid solution is allowed to stand after the addition of the electrolyte and before the amount of coagulation is measured. Burton † allowed the solutions which he examined to stand ten hours: and again ‡ the more dilute solutions which he examined were left for "some days." Weiser and Nicholas § allowed the solutions under examination to stand for twenty-four hours.

In some preliminary experiments the writer found that abnormal results were obtained with a dilute solution owing to the fact that the time elapsing before examination was too short to permit of coagulation with the minimal quantity of electrolyte. This led to an examination of the actual rate of coagulation. Two solutions were employed, one being ten times more dilute than the other. The results were as follows:—

* Borjeson, *Koll. Zeit.* xxvii. p. 18 (1920).

† Burton and MacInnes, *Jour. Phys. Chem.* xxv. p. 517 (1921).

‡ Burton & Bishop, *Jour. Phys. Chem.* xxiv. p. 703 (1920).

§ Weiser and Nicholas, *Jour. Phys. Chem.* xxv. p. 742 (1921).

SERIES I.

10 c.c. of Mastic Dilution 100 per cent. Precipitant $Al_2(SO_4)_3$.

Time after Mixing.....	6 hours.	24 hours.	144 hours.
19.00 millimols./litre	Slight settling	Clear with large floccs	Clear
1.90 "	Clear with large floccs	"	"
1.14 "	"	"	"
.76 "	Not completely clear	"	"
.61 "	"	"	"
.48 "	No change	"	No change
.30 "	"	"	"
.15 "	"	"	"

SERIES II.

10 c.c. of Mastic Dilution 10 per cent. Precipitant $Al_2(SO_4)_3$.

Time after Mixing...	6 hours.	24 hours.	48 hours.	72 hours.	96 hours.	144 hours.
19.00 millimols./litre	No change	Not completely clear	Clear with large floccs	Clear	Clear	Clear
1.90 "	"	"	"	"	"	"
.76 "	"	Slight settling	Not completely clear	"	"	"
.61 "	"	"	Slight settling	Not completely clear	"	"
.46 "	"	"	"	"	"	"
.38 "	"	"	"	"	"	"
.30 "	"	No change	No change	No change	No change	Slight settling
.22 "	"	"	"	"	"	"

It is obvious that the rate of coagulation decreases considerably with decreasing concentration of the mastic. The point of complete coagulation was taken to be "clear with large flocks." These flocks do not necessarily settle to the bottom of the vessel; some adhere to the side. The interior of the liquid, however, appears quite clear. It is noticeable that the flocks adhering to the sides are more numerous upon, if not confined to, the side of the vessel away from the source of daylight illumination.

It is apparent that, in order to arrive at the point of complete coagulation in the case of the more dilute solution, it is necessary to leave it undisturbed for a good many days, a course of action to which there are several objections, apart from that of mere convenience, in carrying out a series of numerous determinations. During this time external influences, such as chemical action at the surface of the particle, have more time to show themselves.

These objections can be obviated by centrifuging the solution after a definite time at a constant speed. The rate of coagulation is made up of two factors, the rate of aggregation of the particles and that of settling of the aggregates so formed. By centrifuging, the influence of the latter is reduced to a minimum, and we arrive at a truer measure of the former. An examination of this method shows that it is possible to obtain complete coagulation after a reasonable length of time.

The solutions were treated in the way to be described, and the following tables (and figs. 1 and 2) show the minimal concentrations of $\text{Al}_2(\text{SO}_4)_3$ and NaCl at various intervals after the moment of addition for complete coagulation. Similar results were obtained with BaCl_2 .

It will be seen that the minimal concentration of electrolyte decreases rapidly with time until from 12 to 22 hours after mixing, thereafter, it remains fairly constant. In order, however, to ensure reaching the true end-point, the solutions in the subsequent experiments were allowed to stand 48 hours after mixing and before centrifuging.

Several workers have pointed out that the rate and method of addition of the electrolyte affect the end-point. Weiser and Middleton* devised an apparatus, by the use of which they obtained concordant results, and a modification of it made by the writer was found to give equally good results. In order to ensure perfect cleanliness, it was made of glass throughout. The modified apparatus consisted of

* Weiser and Middleton, *Jour. Phys. Chem.* xxiv, p. 30 (1920).

SERIES III.

Rate of Coagulation of Mastic with $\text{Al}_2(\text{SO}_4)_3$.

Time after Mixing	15 minutes.	60 minutes.	5 hours.	15 hours.	25 hours.	48 hours.
Limal Concentration of $\text{Al}_2(\text{SO}_4)_3$						
Dilution 100 p. c.	> 20 millimols.	> 20 millimols.	1.04 millimols.	.38 millimols.	.38 millimols.	.38 millimols.
" 10 "	> 20 "	> 20 "	"	.23 "	.15 "	.15 "
" > 20 "	> 20 "	> 20 "	> 20 "			

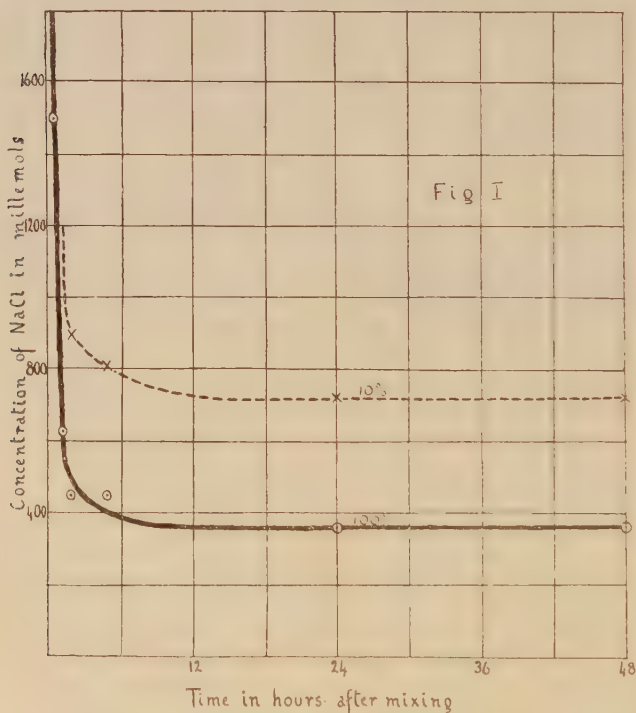
SERIES IV.

Rate of Coagulation of Mastic with NaCl.

Time after Mixing	30 minutes.	45 minutes.	2 hours.	5 hours.	24 hours.	48 hours.
Liminal Concentration of NaCl. } Dilution 100 p. c. Ca. 1500 millimols. " 10 " >1500 " >1500 " 900 " 810 " 720 " 720 "						

two vessels, one slightly smaller than the other, and fitting by a ground-in joint inside the larger.

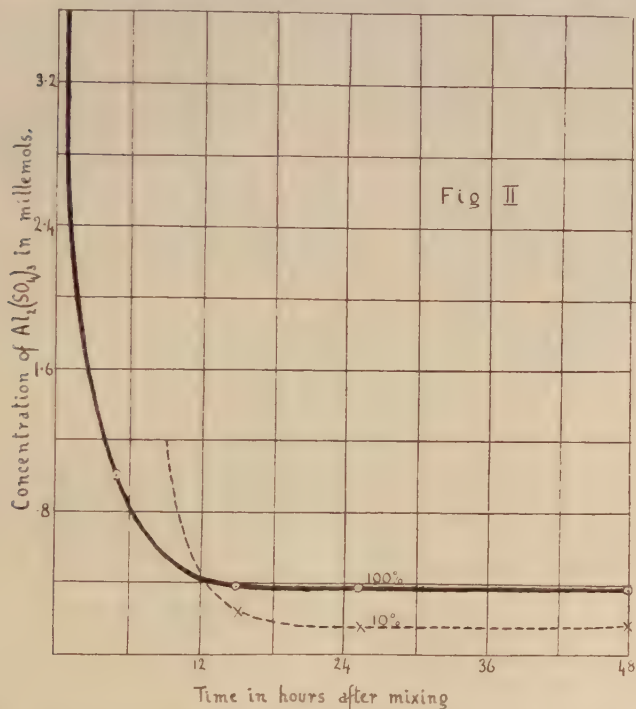
The smaller vessel has a slightly higher inner cylindrical vessel, the base of which is concentric with that of the outer vessel and fused to it. The electrolyte solution is placed in the inner vessel and the colloidal solution in the annular space, both having been previously rinsed out with their respective solutions. The larger vessel is placed over the smaller, and the whole inverted and left for 30 seconds



to drain. By this means a sudden and complete mixing of the two solutions is obtained. The mixed solution is then poured into a vessel of hard glass and corked. The whole apparatus, as were all the vessels with which the mastic solution came in contact, is made of hard glass and was steamed out between each series.

The experiments were conducted with 10 c.c. of the mastic solution at the required dilution. Into the inner vessel was poured enough water to make the volume of the electrolyte solution up to 5 c.c., and then the latter solution was added at a convenient concentration. To determine

one end point for a given concentration of mastic and a given electrolyte, four solutions were made up with a fairly wide difference of concentration in each solution, so as to give a large bracket. After standing 48 hours and centrifuging for half an hour at 2000 r.p.m., at which speed there was no sedimentation of the pure mastic solution, four more solutions were made up, in which the concentrations of electrolyte were such as to cover the interval between the



two concentrations in the first determination, within the limits of which the end point was observed to lie. The process was repeated until the limit of observation was reached, and eventually gave two concentrations of which it was possible to say that one definitely caused complete coagulation, and one did not. The end point was taken as the mean of these two concentrations. The observation of the solutions was made by daylight against a black background. The size of the final bracket of concentration varied directly with the concentration of electrolyte necessary for coagulation, and the results were therefore more accurate with trivalent ions than with monovalent. The results were as follows (Series 5, 6 and 7, and figs. 3, 4 and 5).

SERIES V.—Coagulant $\text{Al}_2(\text{SO}_4)_3$.

Final Concentration of Mastic.	66.7 p. c.	53.3 p. c.	40 p. c.	33.3 p. c.	26.7 p. c.	20 p. c.	13.3 p. c.	6.7 p. c.
Liminal Concentration of $\text{Al}_2(\text{SO}_4)_3$ in millimols. { Soln. B. Fr. II. Fr. VI.29	.27	.25	.24205	.170	.115 (?)
	.27	.24	.21	.200	.170	.140	.090	...
	.29	.27	.24	.205	.175	.145

SERIES VI.—Coagulant BaCl_2 .

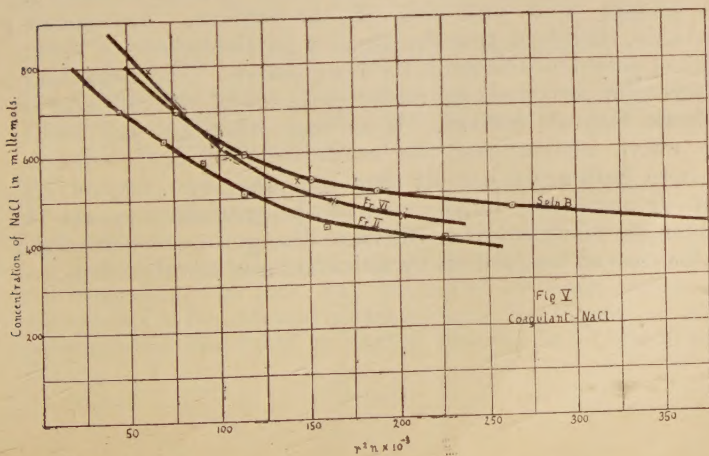
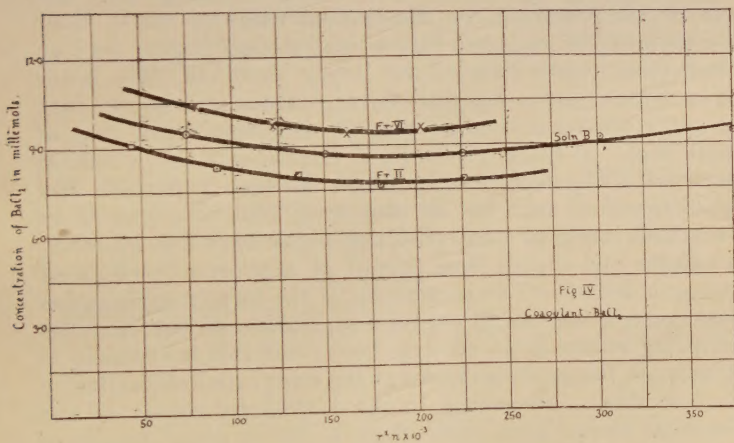
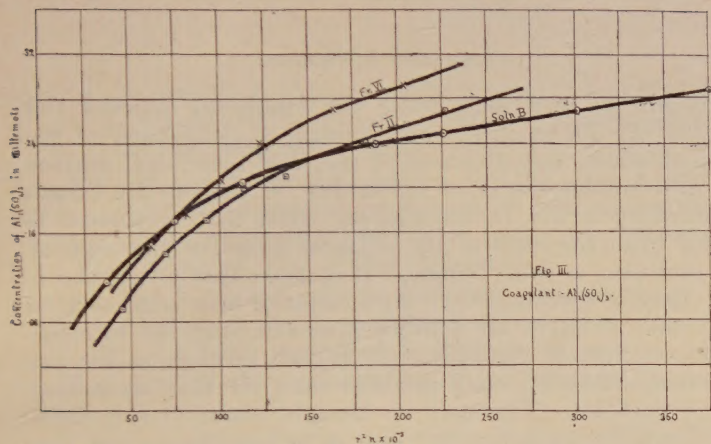
Final Concentration of Mastic.	66.7 p. c.	53.3 p. c.	40 p. c.	26.7 p. c.	13.3 p. c.
Liminal Concentration of BaCl_2 in millimols. { Soln. B. Fr. II. Fr. VI.	9.5	9.3	8.8	8.8	9.5
	7.9	7.7	8.1	8.3	9.1
	9.6	9.4	9.7	10.4	...

SERIES VII.—Coagulant NaCl .

Final Concentration of Mastic.	66.7 p. c.	53.3 p. c.	46.7 p. c.	33.3 p. c.	26.7 p. c.	20 p. c.	13.3 p. c.
Liminal Concentration of NaCl in millimols. { Soln. B. Fr. II. Fr. VI.	430	...	470	510	540	600	700
	400	...	430	510	580	630	700
	450	490	540	610	690	790	...

Interfacial Surface.

Final Concentration of Mastic.	66.7 p. c.	53.3 p. c.	46.7 p. c.	40 p. c.	33.3 p. c.	26.7 p. c.	20 p. c.	13.3 p. c.	6.7 p. c.
$r^2 \times n \times 10^{-3}$ { Soln. B. Fr. II. Fr. VI.	376	301	263	226	188	151	113	75	38
	226	181	159	136	113	91	68	45	23
	204	164	143	123	102	82	61	41	20



Discussion of Results.

It will be seen that, under the conditions imposed and within the limits of the experiments, a comparison of the data obtained, upon the basis of the total interfacial surface in unit volume, leads to uniformity in the curves. Such uniformity is not to be observed when the comparison is based upon the mass of the disperse phase, or the number of particles, in unit volume. It appears that adsorption is very largely conditioned by the amount of interfacial surface exposed. It is to be noticed, however, that the minimal concentration of electrolyte is higher throughout for the fraction containing small particles than for that containing large particles. This may be brought about in two ways. The smaller particles may bear a higher charge per unit area of their surface, or the critical value to which their charge must be reduced before coagulation begins may be lower than in the case of the larger particles. The latter explanation is more probably correct, since it is known that the surface tension of large particles is greater than that of small ones. It seems probable, if the existence of a critical potential difference for coagulation between a particle and the dispersion medium be admitted, that this should be lower in the case of small particles which have less tendency to adhere, and should thus permit of a greater freedom of approach between the particles. If the former explanation were correct, we should expect a separation of the particles according to size in an electric field; but this is contrary to experience, the particles move at the same rate independently of their size. According to the Helmholtz theory of the electrical double layer, this effect is due to equal density of the charge upon unit area of the surface. It appears probable, therefore, that the smaller particles have a lower critical potential difference for coagulation. The behaviour of the solution containing mixed particles of different size is in some respects curious. With both $\text{Al}_2(\text{SO}_4)_3$ and NaCl the curve representing the coagulation of this solution is more flattened relatively than the other two curves. A lack of uniformity in the size of the particles appears to render the solution less sensitive to change in concentration, in the case of coagulation by univalent and trivalent ions.

Summary.

- (a) A separation of the particles present in a suspension of gum mastic has been effected by Odén's method of fractional coagulation.
- (b) The density of the particles, and the mass of mastic and the number of particles in unit volume have been measured, and from them the interfacial surface in unit volume calculated.
- (c) The variation of the minimal concentrations of $\text{Al}_2(\text{SO}_4)_3$, BaCl_2 , and NaCl to coagulate solutions containing particles of different mean size with change in concentration of the solutions has been investigated.
- (d) It has been shown that uniformity in comparison of the results can be obtained upon the basis of the interfacial surface in unit volume. It has also been shown that, upon this basis of comparison, small particles require a higher minimal concentration of electrolyte than large particles.

In conclusion I should like to thank Dr. A. S. Russell for his valuable advice and assistance, and Mr. H. M. Carleton for kindly putting at my disposal the microscopical apparatus required.

Christ Church Laboratory, Oxford,
May 15th, 1922.

XII. *Notices respecting New Books.*

Basic Slags and Rock Phosphates. By G. SCOTT ROBERTSON.
Pp. xiv + 112, 8 plates. 1922. Cambridge Agric. Monographs.
Cambridge University Press. 14s. net.

THE value of scientific investigation of the results accruing from the use of phosphatic dressings on crop-production is obvious to all, but it gains in emphasis when, as Sir E. J. Russell points out in a preface to the above book, agriculturists have to realize that the composition of basic slag has undergone much change in consequence of the enforced modifications in the processes of steel manufacture. We would go farther than Sir E. J. Russell and

say that even if the war had not given an impetus to the change over from the basic Bessemer and acid open-hearth processes, economic considerations would none the less have demanded the development of the basic open-hearth production of steel from low-grade iron-ores. "This result" (to quote from the preface) "is, of course, distinctly awkward for the agriculturist who sees a valuable fertilizer disappearing, and being replaced by one which is more costly and at first sight seems to be nothing like as good."

After a review of the various scattered experiments on the use of rock phosphates and basic slags hitherto undertaken, Dr. Scott Robertson describes in detail the Essex experiments carried out in the winters of 1915, 1916, 1918, and 1919 under the auspices of the East Anglian Institute of Agriculture. The soils treated were those of the Chalk, London Clay, and Boulder Clay, and varied considerably in mechanical and chemical composition. The yields of hay and clover were correlated with the rainfall, and it was found that the drier the season, the greater was the increase in production due to the use of phosphates. The botanical results are also given, the crowding-out of the weeds and the covering of bare areas with grass being noteworthy. Dr. Robertson's main conclusion is that for root crops and late harvests with high rainfall, rock phosphates will prove a suitable substitute for the high-grade Bessemer basic slags. The careful records and correlations were made personally by Dr. Robertson at considerable inconvenience and discomfort, and under most difficult circumstances. They are therefore the more valuable, and do him the greater credit.

The latter part of the book is concerned with investigations of the large yields resulting from the use of basic phosphates. From botanical analyses it is evident that the open-hearth fluor-spar slags of low solubility are less effective than the non-fluor-bearing and therefore more highly soluble slags. The effects of the temperature and texture of the soil on the accumulation of nitrates, on the soil bacteria, and on the acidity and lime-requirement are clearly expounded, and the deductions emphasized by means of abundant statistics.

Altogether, the work constitutes a most valuable contribution to agricultural knowledge. It is a pity that the publishers cannot retail this book of 112 pages and 8 plates for less than 14s.

P. G. H. B.